New insights into aging phenomena from plasma chemistry

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Abstract

While gas discharges under atmospheric pressure occur as filamentary discharges, most studies on plasma polymerization, or plasma Chemical Vapor Deposition, were carried out in low-pressure (low-temperature, non-equilibrium) plasma. However, it is reasonable to assume that the fundamentals of plasma polymerization found by low-pressure discharge apply to the gas phase in the filamentary discharge. Plasma polymerization as a potential cause of aging effects is reviewed with respect to (1) polymerization in DC discharge, (2) competitive ablation and polymerization principle, and (3) from the viewpoint of detector wire aging.
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1. Introduction

If a gas, which has high tendency to polymerize in the environment of electrical discharges, is used in a gas detector system, so-called "aging effects" would be seen very quickly because the detection wire would be coated by the deposition of a "plasma polymer" when gas discharges occur. From this point of view, it is mandatory to use gases, which do not polymerize in the environment of electrical discharges. On the other hand, many organic compounds, which are not considered as monomers (starting materials) for polymerization, polymerize in plasma. A mixture of two gases, which do not polymerize when used as single gases

in a plasma, can polymerize in certain cases. Some gases, which are inadvertently introduced to the system, could polymerize under the conditions of gas discharges. Consequently, the selection of gas cannot be made primarily based on the structure of molecules. Thus, some knowledge of plasma polymerization becomes important to understand the very complicated phenomena of "aging effects".

Formation of materials in plasmas is dealt with as plasma polymerization or plasma chemical vapor deposition (PCVD). Plasma polymerization was investigated mainly in low-pressure plasma, or glow discharge. It is generally held that the main luminous body of glow discharge is more or less uniformly in a non-equilibrium plasma state, in which the electron temperature is much higher than the temperature of ions and of neutrals. This is not an accurate description of glow discharge in

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a strict sense, and glow discharge is not at all uniform within the luminous glow, which could be identified as a low-pressure plasma, and the nature and the amount of materials deposited differ significantly within the more or less uniform plasma. The non-uniformity within a low-pressure plasma could be viewed as an "onion structure". The more or less uniform plasma surrounds an electrode or a substrate like a layer of an onion, but the next layer is slightly different from the first one, and so forth.

The recognition of a more or less uniform plasma is important when dealing with electrical discharge that occurs under atmospheric pressure. If the system pressure of the low-pressure plasma described above is increased, the difference between the electron temperature and temperature of ion and neutrals becomes small, and it is generally recognized that these temperatures become the same and the (more or less uniform) plasma becomes an equilibrium (hot) plasma. It is unlikely that such a hot plasma fills the gas phase of a detector.

Under higher pressure, e.g. atmospheric pressure, the breakdown of the gas phase could occur as a narrow path of discharge without converting the whole volume of gas into a hot equilibrium plasma. Corona discharge under atmospheric pressure, for instance, occurs as filamentary discharge, which is significantly different from large-volume luminous glow discharge. Within a filamentary discharge, which occupies a very small fraction of the gas phase under consideration within the duration of a single occurrence, it could be assumed that the gas phase is similar to that of a low-pressure discharge but not that of a hot plasma, which could melt or vaporize many materials. Because of the filamentary nature of the discharge, however, the influence of such a discharge to the material is limited to a small area where the discharge strikes. Lightning during a thunderstorm is a typical model of filamentary discharge under atmospheric pressure. The damage of a lightning is limited to the spot where the lightning strikes. In filamentary discharges, the onion structure of a more or less uniform plasma phase does not exist.

The frequency of occurrences of a filamentary plasma can be increased under certain conditions. For instance, a so-called "atmospheric glow discharge" is created in the atmospheric gas phase between insulated electrodes separated approximately 2–3 cm and filled with helium. Argon mixed with a small amount of acetone or some other discharge-enhancing gas seems to create such "atmospheric glow discharge". Such a description only refers to the appearance of the discharge, and the nature of the discharge is still that of a filamentary discharge. If lightning is struck every second, the sky would appear as if it were in glow discharge. Such discharges have been used to modify the surface characteristics of polymer films and fibers, implying that "atmospheric glow discharge" is not a glow discharge under high pressure, which should be a hot plasma.

Most fundamental research in low-pressure plasma was driven by applications in plasma etching and material deposition for microelectronics industries, and also by needs for surface modification and nano-film coatings for larger-sized materials. In so far as fundamental research on plasma polymerization is concerned, atmospheric discharges have major drawbacks in (1) the limited size of space in which a discharge can be created, and (2) much larger amounts of gases (e.g. 1000 time more than for low-pressure discharge) are needed, which becomes a major drawback for expensive gases and organic compounds.

Potentially damaging effects of plasma exposure, particularly in filamentary discharges, are (1) deposition of materials on the wire, (2) chemical reactions of reactive species created in plasma, and also (3) the damage caused by the impact of energetic electrons (on the anode) and ions (on the cathode). The material deposition is not solely caused by the gas used, but any volatile component emanating from any materials used in the entire system, including sealant, adhesives, and piping materials, could act as monomers of plasma polymerization. Understanding of the overall effects of plasma on a material surface investigated by low-pressure plasma is believed to provide new insight into the aging effect of the wire used in gas detectors.

2. Glow discharge and plasma polymerization investigated by DC discharge

Although most research on plasma polymerization was done with high-frequency discharges, (kHz–GHz), a DC discharge might be closer to the phenomena involved in the problems related to wire aging. While basic studies of DC-discharge polymerization were reported in the dawn of plasma polymerization in the early 1960s, DC-discharge polymerization has not been a favorite mode of plasma polymerization, probably due to the practical utilization of plasma polymerization being focused on the coatings of dielectric materials. In recent years, however, the importance of plasma polymerization in corrosion protection of metals was recognized, and it was found that DC polymerization is an ideal method because the metallic substrate to be coated can be used as the cathode for a DC discharge [1–6]. DC-cathodic polymerization was found to be significantly different from glow discharge polymerization in high-frequency discharge [7], and some findings by DC-discharge polymerization provided a broader view of plasma polymerization than what had been constructed based on the results of high-frequency discharge polymerization alone. Recent findings by DC-discharge polymerization are briefly summarized below.

2.1. Creation of chemically reactive species in a DC discharge

The foundation of the chemistry of plasma polymerization and of plasma treatment of material surfaces is based on the chemical reactions of reactive species created by the dissociations of organic molecules caused by the impact of electrons, ions, and exited neutral species in the plasma. Although the primary species created by the ionization of organic molecules or fragmented moieties may not play the dominant role, it is quite clear that the whole process does not proceed without the ionization process. Therefore, it is important to recognize the fundamental step of ionization in a gas discharge system. For this purpose, the simplest case of ionization of argon in a DC glow discharge has been used in explaining the fundamentals of a glow discharge.

In a DC-discharge plasma polymerization reactor, a constant voltage is applied between a cathode and an anode, and the luminous glow develops near the cathode surface. The maximum of the electric field exists near the surface of the cathode, and the acceleration of electrons mainly takes place in this region. The ionization of an argon atom occurs when an electron gains sufficient energy to ionize the atom. Therefore, the ionization of argon takes place in the vicinity of the cathode glow.

The distribution of electron temperature (energy of electrons) and number of electrons in a DC argon glow discharge in a plasma polymerization reactor is shown in Figs. 1 and 2, respectively [8]. The data shown are taken on a plane at the center of the electrode which is perpendicular to the two electrodes (cathode and anode).

The electron temperature rises as electrons are accelerated in the electric field. During this process, the number of electrons is relatively small. When the electron temperature reaches the maximum level as a function of the distance, T_e starts to drop significantly, but the number of electrons starts to increase as electrons are pulled towards the anode. The positively charged argon ions will be pulled towards the negatively charged cathode
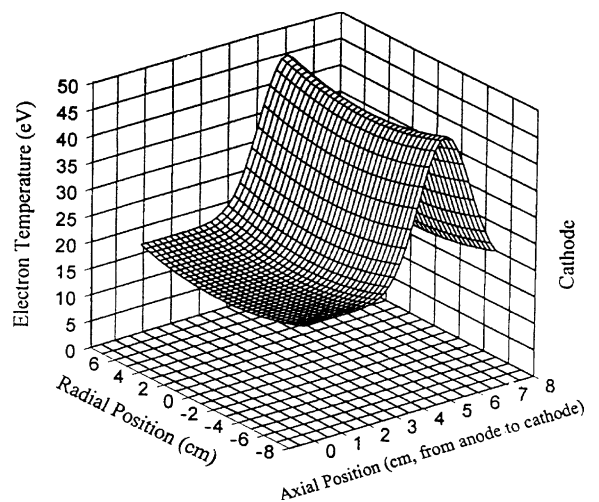

Fig. 1. Distribution profile of electron temperature in an argon DC glow discharge in a plasma polymerization reactor.
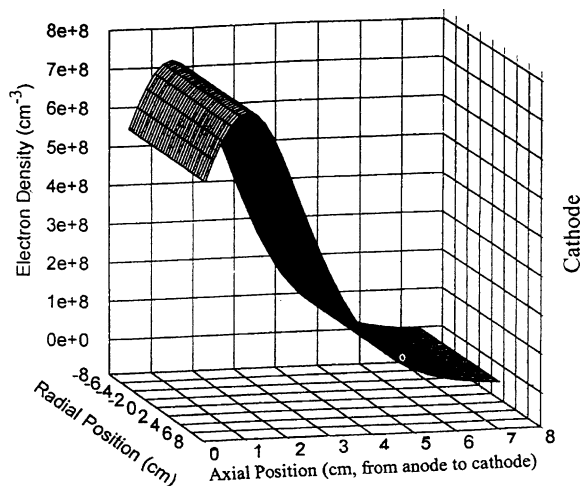
Fig. 2. Distribution profile of electron density in an argon DC glow discharge in a plasma polymerization reactor.

surface and cause the emission of secondary electrons, which will be accelerated while traveling in the cathode fall region. Beyond the cathode fall region, very little electric field exists and no significant acceleration of an electron occurs. The major portion of the negative glow is filled with a large number of electrons, whose energy is not high enough to ionize a significant amount of argon but high enough to create argon atoms in various excited states.

With organic molecules, the consequence of ionization is much more complex than the simple case of the argon glow discharge shown. However, the movement of electrons can be considered to be similar to the case shown for argon glow discharge. In so far as plasma polymerization (PCVD) is concerned, the location where the creation of reactive species occurs and its relative position to the substrate surface, on which plasma polymers are deposited, are important factors to be considered.

The well-characterized DC glow discharge is more or less limited to the discharge of inert gases. When an organic gas, instead of an inert gas, is used in the same discharge reactor, a nearly completely different phenomenon occurs, in which the deposition of material occurs and the composition of the gas phase changes continuously as

deposition proceeds. This difference can be further illustrated by examples for glow discharge of argon and of acetylene.

In a closed system, e.g. 500 mTorr of argon or acetylene, the discharge is completely different in the following way. The glow discharge of argon can be maintained indefinitely, and diagnostic measurements such as electron temperature measurement and emission spectroscopy could be carried out in such a steady glow discharge. In contrast to this situation, the glow discharge of acetylene extinguishes within a few seconds to a few minutes depending on the size of the tube and the system pressure. This is because acetylene forms polymers and deposits on the wall of the reactor. In the process of plasma polymerization of acetylene, very little hydrogen, or any gaseous species, is created, and the plasma polymerization acts as a vacuum pump. When the system pressure decreases beyond a certain threshold value, the discharge cannot be maintained.

A similar situation can be also seen in a flow-system discharge. Again argon discharges can be maintained indefinitely under a steady-state flow of argon under a given pressure. This is not the case with acetylene glow discharges. At a relatively low flow rate, e.g. 1 sccm, and when the pumping rate is not controlled to adjust the pressure change, e.g. under full pumping capacity, the acetylene is consumed (by plasma polymerization) faster than it is replenished by the flow of acetylene. Consequently, the system pressure decreases, and the glow discharge extinguishes. In a flow-system, however, acetylene is fed into the system continuously at a given flow rate, and the system pressure increases as soon as the glow discharge extinguishes. As the system pressure increases back to the pressure, where breakdown of the gas phase could occur under the applied voltage, glow discharge is ignited again, but the re-ignited glow discharge follows the same path of the first discharge. As a consequence of these processes, the glow discharge occurs as a self-pulsating intermittent discharge.

A significant difference between glow discharge of an inert gas such as argon and that of an organic compound such as acetylene is the fundamental step of creating excited or reactive

species. The low energy electron on the slope of increasing energy shown in Fig. 1 is energetic enough to dissociate the organic molecule ("electron impact dissociation"). Thus, the direct ionization of the entire molecule is rather an unlikely event while such a step should be the major and the most important step, if one applies the fundamental knowledge gained by argon discharges without modifications to account for the basic difference. The ionization would occur with fragmented moieties in the case of organic gases.

Species that contribute to the deposition of materials in the cathode region are mainly created by the electron impact dissociation in the cathode dark space. Ions are pulled to the cathode surface by the electric field. As the energy increases as an ion travels towards the cathode, neutral species, including the monomer, could be dissociated by the ion impact dissociation. The polymer forming (reactive) species thus created in the dark space near the cathode are not photon-emitting species [9]. This aspect is also evidenced by the reduction of the intensity of luminous glow when an organic gas is added to an argon discharge, and also by the fact that the glow discharge of a fast-polymerizing gas such as acetylene is associated with very faint glow.

Polymer-forming species thus created in the cathode region of a DC discharge, presumably free radicals and cation-free radicals, are deposited on the cathode surface and form a solid film by reacting with the substrate surface and each other. In order to maintain glow discharge, however, the secondary electrons must be emitted from the cathode surface. This means that the secondary electrons must come out of the cathode surface, which could be sufficiently covered by the deposited plasma polymer. The emission of secondary electrons from the surface of dielectric materials is a well-known phenomenon. In the case of plasma polymers, it can be understood that the surface-state electrons, which are responsible for the contact electrification of the polymer surfaces (static charges), could be emitted as the secondary electrons to sustain the glow discharge. An ultra-thin layer of plasma polymer (up to ca. 100 nm) is electrically conducting as evidenced by the fact

that a plasma coated metal plate can be coated by the electrochemical deposition of paint (E-coating) [1]. Thus the plasma polymer layer remains at the same electrical potential of the cathode (within a limited thickness) and the work function for the secondary electron emission does not increase significantly.

Another important factor is the negative glow in a DC discharge, which is observed both in argon and acetylene glow discharge. The negative glow constitutes the main body of glow in which plasma polymerization of organic vapors generally occurs in high-frequency discharges. The negative glow in a DC discharge should also cause plasma polymerization of an organic vapor. The mechanisms of the creation of polymer-forming species in the negative glow must be significantly different from that for the cathodic polymerization described above. While the ionization is essential for sustaining the glow discharge, the reactive neutral species (free radicals), which can be considered as the byproducts of the ionization, are dominant species that control the deposition of an organic compound in plasma [10].

The above explanation of the difference between DC glow discharges of an inert gas and of an organic vapor is a speculative one. However, the deposition data support the concept of the dark-space polymerization. The difference in the deposition kinetics in the negative glow and in the cathode dark space, which will be described in detail in the following sections, strongly indicates that the cathodic deposition is not the deposition of species that are created in the negative glow and enhanced by the electric field in the cathode fall.

The glow discharge initiated by an alternating current power source can be visualized by an alternating cathode and anode shown in the DC glow discharge, up to a certain frequency, e.g. 50 kHz. Therefore, the polymer deposition in a DC discharge as well as in an alternating current discharge is a mixture of DC-cathodic polymerization that occurs in the cathode dark region and *plasma polymerization* that occurs in the (negative) glow.

At a higher frequency (e.g. over 100 kHz), an electron can no longer travel the distance to reach the anode within a cycle, and consequently the

oscillation of electrons becomes the major motion of electrons in 13.56 MHz and microwave discharges. In this case the collision of an oscillating electron with an atom or a molecule is the principal mechanism of ionization as well as the creation of polymer-forming species, which occur away from the electrode surface. Thus, the predominant role of the cathode observed in DC and alternating current discharge would diminish in 13.5 MHz discharge.

2.2. Deposition rate as a function of operation parameters

The formation of reactive species and the deposition of materials from these in the cathode region can be termed *cathodic polymerization* and those occurring in the remainder of the space can be plainly termed *plasma polymerization* for the purpose of discussion. According to this distinction of two processes, the *cathodic polymerization* takes place in the "dark" space, and the *plasma polymerization* occurs in the "glow". It should be clarified that "dark" and "glow" merely refer to the location where plasma polymerization takes place. Polymerization does not emit photons because the excess energy is dissipated in the chemical reactions to form polymers. Polymerization and photon-emission are both deactivation processes of excited species and compete with each other in the plasma process.

2.2.1. Deposition in plasma

In the *plasma polymerization*, the activation (formation of the reactive species) and deactivation (deposition of materials) are coupled, because the power input is directly applied to monomer gases and the polymerization occurs mainly in the glow region of a reactor. In essence, the activation of an organic molecule for the "glow" polymerization starts at the boundary of glow. The supply of the monomer into the glow volume is a crucially important factor because the monomer is consumed in the glow by depositing polymers and the numbers of polymer-forming species in the glow decreases. It has been well established that the *plasma polymerization* is primarily controlled by a composite power parameter, W/FM, where W is

the discharge power in Watts, F is the volume (or molar) flow rate, and M is the molecular weight of the monomer. W/FM represents the energy input per unit mass of the monomer, which is given in J/kg [10].

As the power input is increased (at a given flow rate), the domain of plasma polymerization approaches the monomer-deficient one, which can be recognized by the asymptotical approach of the normalized deposition rate to a horizontal line as the power input increases. In the monomer-deficient domain, the deposition rate (asymptotic value) will increase as the flow rate is increased and will show a linear dependence on the monomer feed-in rate at a given discharge power and system pressure. It is important to note that the deposition rate depends on the composite parameter W/FM. Consequently, an increase in flow rate (at a given discharge power) has the same effect as decreasing the discharge power (at a given flow rate), and conversely, an increase of discharge power has the same effect as decreasing the flow rate.

In the power-deficient domain, the normalized deposition rate, which is given by (deposition rate)/FM, can be expressed by a unique equation of the power input parameter, W/FM. The data to show this relationship are shown in Fig. 3. This figure illustrates how well the thickness growth rate, GR/FM, in 40 kHz and 13.5 MHz *plasma polymerization* of methane and *n*-butane, can be
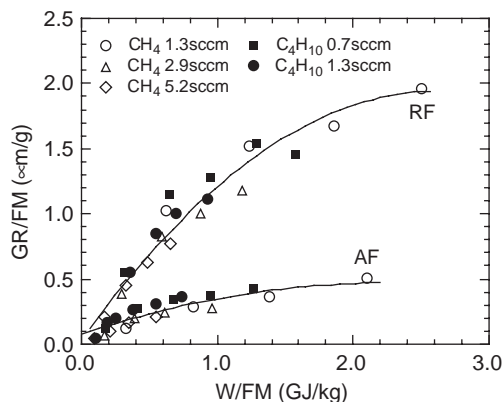

Fig. 3. Dependence of GR/FM on W/FM for 40 kHz and 13.56 MHz plasma polymerizations; flow rate: methane 1.3, 2.9, 5.2 sccm, *n*-butane 0.7, 1.3 sccm.

expressed as a function of the composite input parameter W/FM. It is important to recognize that regardless of the mass of monomer, flow rate, and discharge wattage, a single line fits all data obtained in 40 kHz or 13.5 MHz plasma polymerizations of hydrocarbons, in which the deposition occurs on an electrically floating conductor or on a dielectric substrate placed in the glow. This figure shows the asymptotical approach to the monomer-deficient domain and also points out that the normalized deposition rate differs depending on the nature of the power source employed when an identical experimental setup, except for the power supply, is used.

2.2.2. Deposition in cathodic polymerization

When the same principle for *plasma polymerization* is applied to express the thickness growth rate in *cathodic polymerization*, it becomes quite clear that the cathodic "dark" polymerization is not the "glow" *plasma polymerization*. There is a clear dependence of the deposition rate on W/FM, but no universal curve can be obtained. In other words, the relationship applicable to glow discharge polymerization does not apply to *cathodic polymerization*. The best universal dependency for *cathodic polymerization* is found between (deposition rate)/M and the current density [7]. Fig. 4

depicts this relationship for all *cathodic polymerization* data which were obtained in the same study, covering experimental parameters such as flow rate, size of cathode, mass of hydrocarbon monomers, but at the same system pressure.

The implications of the correlation shown in Fig. 4 are as follows: (1) The energy input parameter (based on the plasma phase) does not control the deposition of material onto the cathode surface. (2) The current density of a DC glow discharge is the primary operational parameter. (3) The flow rate of the monomer does not influence the film thickness growth rate. (4) The film thickness growth rate depends on the mass concentration of monomer (CM) in the cathode region rather than on the mass input rate (FM) [11]. (In these experiments, the system pressure was maintained at a constant value of 50 mTorr, and thus C was a constant.)

In cathodic polymerization, (deposition rate)/CM (not FM) is proportional to the current density. Since the mass concentration of the monomer in the cathode region depends on the system pressure, the deposition rate in the cathode region should depend on the system pressure p. This relationship is a conspicuous deviation from the one for "glow" *plasma polymerization* in which the flow rate rather than the system pressure is the rate-determining parameter and hence the deposition rate is independent of the system pressure (for a given flow rate). This difference in the pressure dependence, can be used as a tool to distinguish the "dark" and "glow" polymerizations.

2.2.3. Deposition on an electrode in alternating current discharges

An electrode in an alternating current discharge is the cathode for half of the deposition time and the anode for the other half of the time. The contribution of the cathodic polymerization can be estimated by examining the system pressure dependence of the deposition rate (at a fixed flow rate). If *plasma polymerization* is the dominant factor, it is anticipated that the deposition rate would be independent of the system pressure. If *cathodic polymerization* is the dominant factor, the rate of deposition onto an electrode is dependent on the system pressure, and the value of the
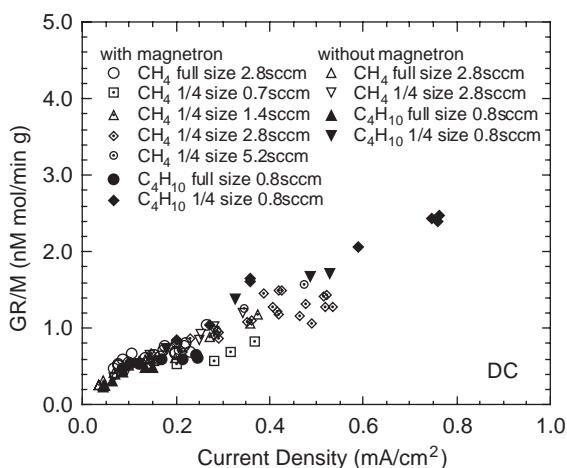

Fig. 4. A master curve for the relationship between GR/M and the current density for DC cathodic polymerization; data obtained under various conditions for methane and *n*-butane.

deposition rate is expected to be one half of that for *cathodic polymerization*.

Trimethylsilane (TMS) deposition rate profiles in DC, 40 kHz, and 13.56 MHz discharges are shown for an electrode in Fig. 5 and for a floating substrate in Fig. 6. It can be seen that, regardless of the frequency of electrical power source used, a uniform deposition of TMS plasma polymers was observed in all three plasma processes. An appreciable edge effect, which is due to the concentration of the electric field on the edge, occurred in the DC plasma and a less pronounced effect occurred in the 40 kHz plasma when the substrate was used as the cathode or powered electrode. The uniform distribution of deposition rates confirms that a reasonably uniform "plasma

state" surrounds the electrode surface, which would not be seen in filamentary discharges, which occur in atmospheric discharges.

With electrically floating substrates, the deposition rates, as well as the refractive indices, are nearly the same for DC and 40 kHz glow discharges. Under the employed conditions, the 13.5 MHz discharge yielded a lower deposition rate, but the refractive index was found to be nearly the same as for the samples formed in DC and 40 kHz discharges. This implies that "glow" *plasma polymerization* in the negative glow of DC and those in 40 kHz and 13.56 MHz are essentially the same. The uniform deposition rate profile indicates the uniformity of the plasma surrounding the substrate in a low-pressure discharge.

The system pressure dependences of the deposition rate onto the electrode surface in DC, 40 kHz, and 13.56 MHz discharges are shown in Fig. 7. As anticipated from the deposition rate equation, the deposition rate of DC cathodic polymerization is linearly proportional to the system pressure [11]. The deposition rate in 40 kHz discharge was found to be pressure dependent also, but in 13.56 MHz it was found to be independent of the system pressure. The deposition rate in the 40 kHz discharge is roughly one half of that in the DC discharge, and the slope of the pressure dependence is also roughly one half of that obtained from DC discharge. These findings indicate that cathodic polymerization takes place on the
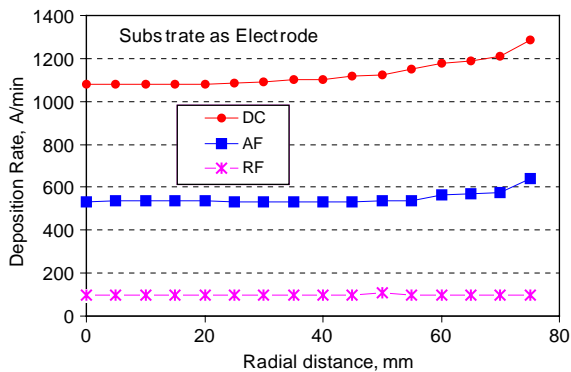

Fig. 5. The deposition rate profiles of TMS in DC, 40 kHz, and 13.56 MHz plasma polymerization processes with substrate as electrode. Plasma conditions are 1 sccm TMS, 50 mTorr system pressure, 5 W power input.
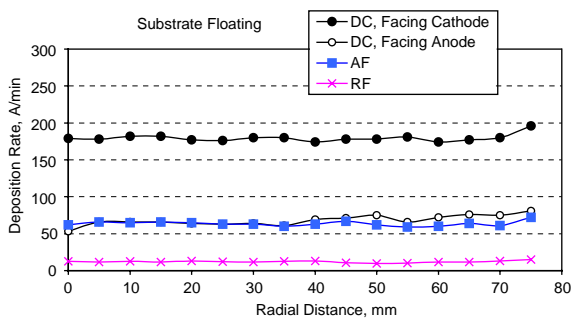

Fig. 6. Deposition rate profiles of TMS in DC, 40 kHz, and 13.56 MHz plasma polymerization processes with substrate floating. Plasma conditions are 1 sccm TMS, 50 mTorr system pressure, 5 W power input.
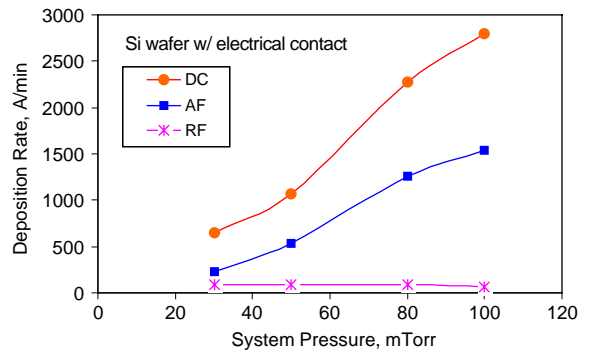

Fig. 7. The system pressure dependence of deposition rate of TMS on Si wafer with electrical contact to the substrate used as powered electrode in DC (cathode), 40 kHz, and 13.56 MHz plasma polymerization processes. Plasma conditions are 1 sccm TMS, 5 W power input.

electrode in a 40 kHz discharge. As the frequency increases to 13.56 MHz, the electrode does not act as the cathode as in DC or 40 kHz discharges, and here the ''glow'' *plasma polymerization* governs the deposition onto the electrode. The species created in the glow are deposited on the powered electrode in a 13.56 MHz discharge.

In order to see the influence of ion bombardment, some silicon wafers were electrically insulated from the substrate plate by placing a thin slide cover glass between the silicon wafer and the substrate. The influence of the electrical contact on the deposition rate onto the electrode and onto the floating substrate is shown in Fig. 8 as a function of system pressure. In the lower part of the figures, the influence of the same factors on the refractive index is shown.

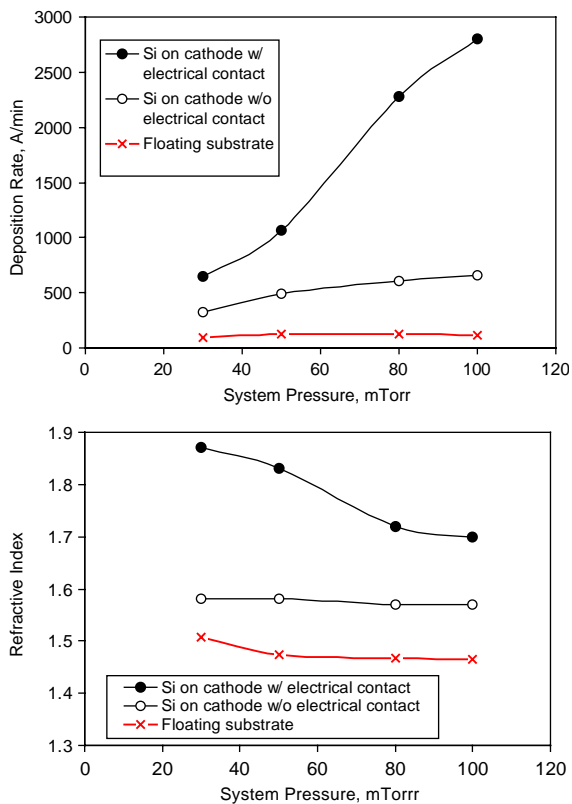In a DC discharge (Fig. 8), without electrical contact, the deposition rate differs significantly from that for *cathodic polymerization* (with electrical contact), and the pressure dependence is marginal. The deposition onto a floating substrate can be characterized as a typical ''glow'' *plasma polymerization*. A major difference in refractive index is seen between the electrode and non-electrode use of the substrates. If one considers that the overall DC plasma polymerization is a mixture of *cathodic polymerization* and *plasma polymerization*, the deposition on the cathode is primarily ''dark'' *cathodic polymerization*. With an insulating layer between the substrate and the cathode surface, there is no cathode dark space, and hence no ''dark'' *cathodic polymerization* that deposits polymers on the substrate. The substrate on the cathode surface without electrical contact or any non-cathode surface receives the products of ''glow'' *plasma polymerization*, which occurs in the negative glow.

2.2.4. Deposition on anode in DC discharge

In a DC discharge, a relatively smaller amount of deposition occurs on the anode surface than what occurs on the cathode. The deposition pattern shows the shape of the cathode, i.e. a rectangular cathode produces a rectangular-shape deposition on a larger square anode. The deposition on the anode surface is not pressure dependent. When a floating substrate is placed between the cathode and the anode, the deposition on the anode shows the shadow of the substrate. The size of the shadow, in which no deposition is observed, is proportional to the size of the substrate that is placed in front of the anode as shown in Fig. 9.

These results indicate that the anode is a passive surface as far as the plasma polymerization is concerned, and the deposition does not differ from the floating substrate placed between cathode and anode, which receives deposition by the ''glow'' *plasma polymerization* in the negative glow region.

Fig. 8. The system pressure dependence of deposition rate and refractive index of TMS in **DC** glow discharge polymerization. Plasma conditions are 1 sccm TMS, 5 W power input.

3. The competitive ablation and polymerization (CAP) principle and plasma sensitivity of elements in plasma polymerization and treatment

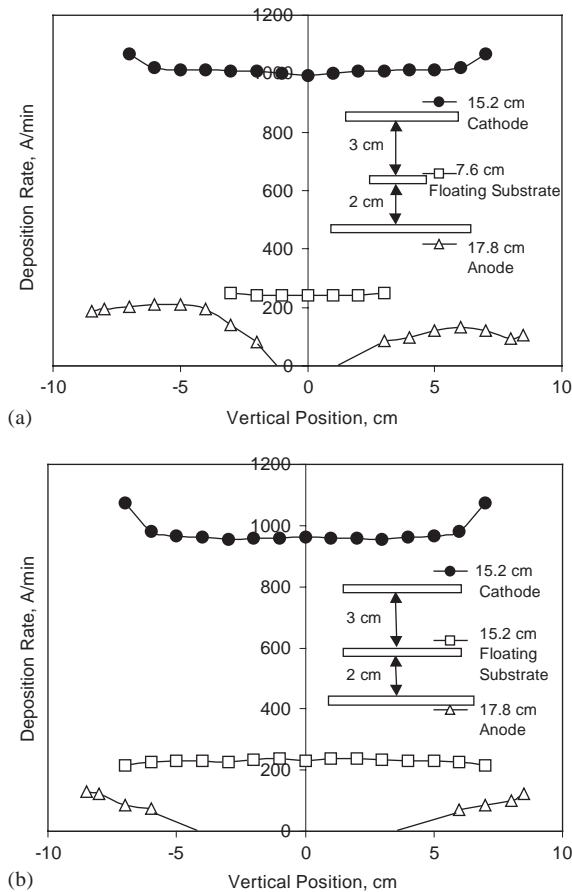The Competitive Ablation and Polymerization (CAP) principle [10] is a basic concept that relates

Fig. 9. The effect of floating panels positioned in front of the anode on the deposition rate on anode surface and cathode surface in DC cathodic polymerization. Conditions are: 1 sccm TMS, 50 mTorr, DC 5 W, anode spacing $d = 100$ mm, $d/2$ is the distance between the cathode and an anode.

the ablation of materials in plasma (gases and solids exposed to plasma) to the deposition of a solid from the plasma phase. Plasma polymerization and plasma treatment cannot be explicated without considering the fragmentation of molecules in both the gas and solid phases. The principle was established by merging two separate observations made in two different plasma processes aimed at mutually opposing objectives. Dr. Eric Kay's group at IBM was working on the etching of Si by perfluorocarbon plasmas. Dr. H. Yasuda's group at the Research Triangle Institute was working on the plasma polymerization of perfluorocarbons.

In the etching study, it was found that when hydrogen was present in a perfluorocarbon plasma etching system, a deposition of materials, instead of etching, was observed [12]. In the plasma polymerization study, it was found that a decrease in the weight of a substrate, rather than a weight increase, was observed when the power-input level was raised above a threshold value [13].

The implication of these findings is that ablation and polymerization could occur in a competitive manner in either plasma etching or plasma polymerization, and the balance depends on the overall system conditions of the plasma, details of which will be discussed in the following sections . Therefore, what happens in a plasma process cannot be determined in an a priori manner based only on the nature of the plasma gas or on the objective of the process. A plasma etching process, such as the pretreatment of an alloy substrate, could result in the deposition of a polymer, and a plasma polymerization process could etch a substrate material. The plasma-sensitivity series of elements involved determines the balance between ablation and polymerization by influencing the fragmentation pattern of molecules in the plasma environment.

Plasma sensitivity refers to the fragmentation tendency of materials and surfaces that come into contact with plasma, which contains various energetic species including ions, electrons, excited species, meta-stables, and chemically reactive species. Bombardment with energetic species such as electron-beams, ion-beams, or X-rays causes much more severe fragmentation than contact with plasma. Plasma sensitivity refers to the latter case rather than sensitivity to ionizing radiation.

The plasma sensitivity series orders the sensitivity of elements to a plasma, in a manner similar to the expression for the ionization of metals in solution by the galvanic series. There is no clear-cut plasma sensitivity series established today. However, there are some trends that seem to be closely related to the plasma sensitivity series. These are trends evident in the order of weight loss rates when polymeric materials are exposed to plasmas [14]. The early recognition of this effect was expressed as the "in–out rule of thumb", which explains that, in a plasma environment,

oxygen has a high tendency to be removed from a molecule, but nitrogen has a tendency to remain in the molecule. This rule was originally outlined in the plasma treatment of polymers; however, a similar rule appears to apply to the fragmentation of gas molecules in plasma.

It is important to recognize that the ionization of a molecule, particularly an organic one, does not follow the same process applicable to a simple mono-atomic gas. The bond energies which link elements are much smaller than the ionization energies of mono-atomic gases used as carrier gases in low-temperature plasma processes. Consequently, the creation of a plasma state of an organic molecule, by itself or with a carrier gas, causes fragmentation of the molecule. The fragmentation of a plasma gas also follows the "in–out rule" that is applicable to a solid organic material.

In order to elucidate the mechanisms by which a polymeric material deposits and also those by which the surface modification of a polymeric material by plasma proceeds, it is vital to comprehend the CAP principle and the plasma sensitivity series. Its updated view was presented recently [15].

3.1. An updated CAP principle

The schematic diagram of an updated CAP principle is displayed in Fig. 10. In this scheme,
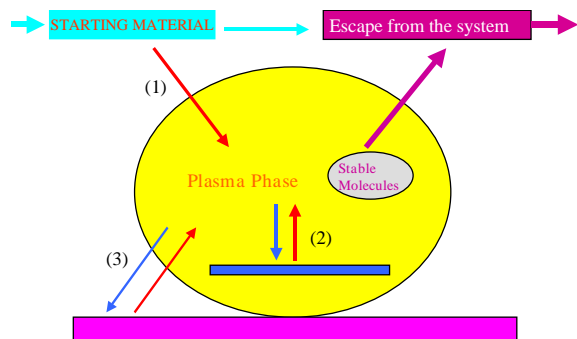

Fig. 10. Schematic diagram of the Competitive Ablation and Polymerization (CAP) principle: (1) ablation of monomer to form reactive species, (2) deposition of plasma polymer and ablation of solid including plasma polymer deposition in plasma phase, (3) deposition to and ablation from non-substrate surfaces (in and out of plasma phase).

there are four major processes necessary to complete the mass balance in the reactor: (1) monomer feed-in, (2) ablation, (3) material deposition, and (4) escape from the system (pump out). The formation of reactive species is an ablation process, because, in general, a considerable amount of fragmentation of the monomer (starting material) occurs.

Material deposition occurs via plasma formation of reactive species; however, it is *not* a simple step of forming a polymeric material from a set of reactive species. The reactive species do not necessarily originate from the monomer, because the ablation process can and does contribute. Gaseous reactive species can originate from once-deposited material (plasma polymer) and also from the reactor wall or any other solid surfaces that are in contact with the plasma.

The following important factors that constitute the CAP principle can be discerned:

1. *Ablation* which is fragmentation, is involved in every process; i.e. monomer to reactive species, plasma polymer to reactive species, wall surface to reactive species, and escape of fragmented species from the system. Fragmentation of molecules is the primary effect of plasma exposure to a material. The importance of ablation can be visualized in the well-established fragmentation patterns of many organic materials, which constitute the foundation of Secondary Ion Mass Spectroscopy (SIMS).

2. The *reactive species* are created not only by fragmentation of the monomer but also by fragmentation of the plasma polymer formed and of materials existing on the various surfaces that come into contact with the plasma.

3. The *escaping species* consist of "non-polymer-forming" stable species and some "un-reacted" monomer depending on system conditions, such as power input level, flow rate, flow pattern, pumping rate, and shape and size of reactor.

4. The *species that do not contribute to polymer formation* are basically stable molecules, such as H_2, HF, and SiF_4. When these species are created in a plasma, the balance between deposition and ablation shifts. However, the manner in which the balance shifts is dependent on the specific system.

The formation of stable escaping species is crucially important in determining the nature of the depositing materials. Some examples, which illustrate the factors described above, are given in the following sections.

3.2. Fragmentation of monomers

The extent of fragmentation in the step from monomer to reactive species can be visualized by looking at the pressure change in a closed-system plasma polymerization of trimethylsilane (TMS) [16], as shown in Fig. 11. In a closed system, an increase in pressure means an increase in the total number of gaseous species, which can be achieved only by fragmentation of the original molecules. In such a system, the composition of the gas phase changes with reaction time as shown in Fig. 12. Accordingly, the composition of deposited polymers also changes with reaction time. This change is evident in the XPS profile of polymer deposition from TMS in a closed system, the pressure change of which is shown in Fig. 11. Fig. 13 contains XPS profiles of plasma polymer deposited in a closed system and of that deposited in a flow system.

With significant or predominant fragmentation of organic monomer molecules, plasma polymerization cannot be considered as molecular polymerization, which links monomer molecules together. This non-molecular nature of plasma polymerization is expressed by the term "atomic polymerization", which may be illustrated by Fig. 14. Plasma polymerization of TMS is a good case to explain the atomic polymerization, because

Fig. 12. Change of gas phase species in plasma of TMS with plasma time. Plasma conditions are: 25 mTorr TMS, 2 panels of Alclad 7075-T6, DC 1000 V.

Fig. 13. C/Si ratios of plasma polymer films of TMS prepared in a flow system reactor (Tfs) and in a closed system reactor (Tcs), as generated by XPS depth profiling.
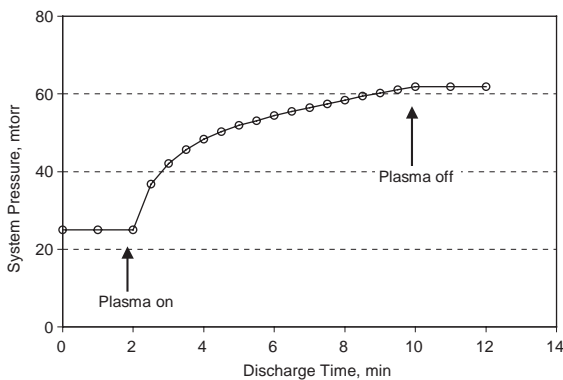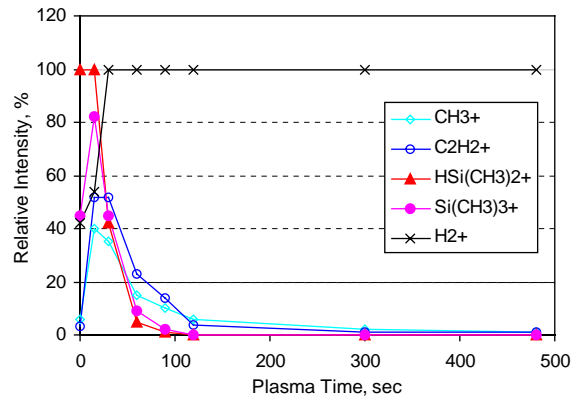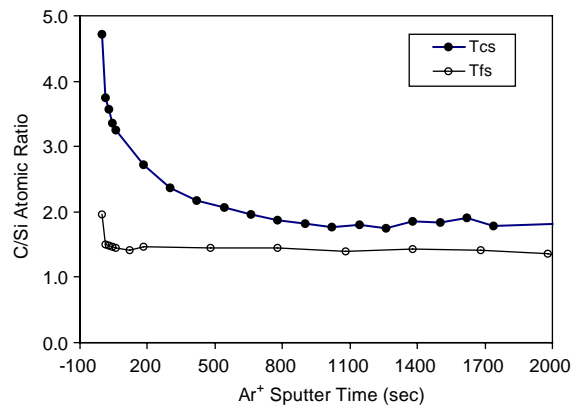

Fig. 11. Increase of system pressure during closed system plasma polymerization of TMS. Plasma conditions are: 25 mTorr TMS, 2 panels of Alclad 7075-T6, DC 1000 V.
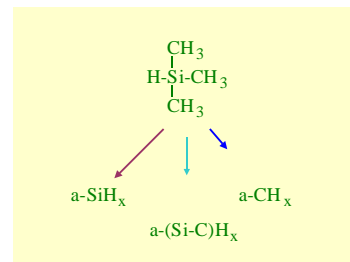

Fig. 14. Atomic nature of plasma polymerization of trimethylsilane (TMS)

TMS has one Si and three C in the monomer molecule, and the characteristic polymerization rates for Si and C differ significantly. How polymeric deposition could be obtained while the original molecules undergo fragmentation was explained by the polymer formation mechanisms shown in Fig. 15, which was explained as a "Rapid Step-Growth Polymerization Mechanism" [10].

As shown by XPS data, cathodic polymerization of TMS in a flow system yields a film structure significantly different from that prepared in a closed system. The film has a graded elemental composition structure starting from Si-rich at the alloy interface to C-rich at the top surface region. This is due to the difference in the characteristic deposition rates of C and Si [17]. Trimethylsilane, $SiH(CH_3)_3$, contains one Si, three C, and 10 H in its original form, and the C/Si ratio is 3.0. In a flow system, the deposited plasma polymer has a very uniform C/Si ratio throughout the film indicating that the gas phase composition does not change with reaction time. This also shows that more Si than C is incorporated into the plasma polymer in a flow-system plasma polymerization. In a closed system, the ratio changes with reaction time, reflecting the change in the composition of the gas phase. This also indicates that Si deposits in the early stages of closed-system polymerization, yielding a Si-poor gas phase. The depletion of Si in the plasma phase is reflected by the sharp increase of the C/Si ratio in the plasma polymer with increased reaction time. These data show how much fragmentation occurs during plasma polymerization and how much influence the fragmentation has on the chemical composition of the resulting plasma polymer.

3.3. Formation of stable molecules in the plasma phase

When stable molecules are formed in the plasma phase, the balances considered in Fig. 10 will shift in a significant manner. An extreme case can be seen in the first observation of polymerization in an etching plasma environment by Kay, et al. [12]. In this case, the formation of HF completely shifts the balance from ablation to polymerization. In the absence of hydrogen, fluorine-containing gases act as effective etching gases for the etching of silicon, because they form stable silicone fluorides, which can be easily removed from the system. When this process is interrupted by the formation of a more stable and easily removable HF in the presence of hydrogen gas, CF_4 plasmas begin to deposit plasma polymer.

When the crucial balance-dictating element comes from somewhere other than the gas phase, the adhesion of a plasma polymer can be seriously damaged. A phenomenon that can be explained in this manner was found in a recent study investigating interface engineering of aluminum alloys [18]. Consecutive plasma polymerization of TMS and then hexafluoroethane (HFE) on an appropriately prepared aluminum alloy surface resulted in excellent adhesion of a primer, which was applied to the surface of the second plasma polymer. As the primer could not be peeled off by any chemical means, obviously, the adhesion of the plasma polymer layers to the substrate metal was excellent. When the plasma reactor was contaminated with fluorine-containing moieties due to a mistake in the operation procedure, extremely poor primer adhesion was obtained for the same coating system, and the primer was easily peeled off of the substrate as a film. This incident provided an opportunity to investigate the interface between the first plasma polymer layer and the substrate metal, since the
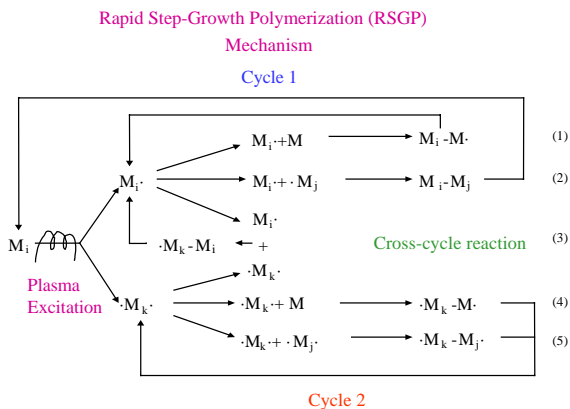

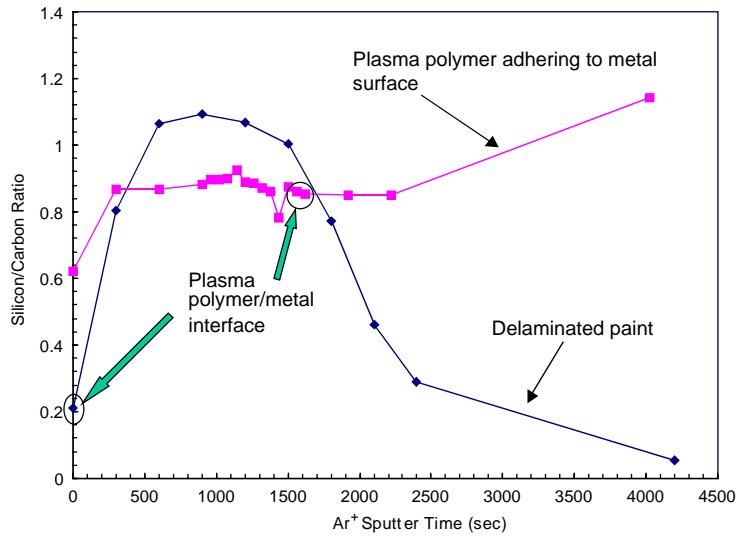Fig. 15. Growth mechanism of plasma polymerization.

Fig. 16. XPS atomic ratio, Si/C, for the failed interface (delaminated paint) and for good adhering interface.

plasma polymers were strongly adhered to the peeled off film.

In Fig. 16, XPS cross-sectional profiles of two plasma polymers are compared: (1) that of the paint that peeled off due to poor adhesion resulting from the interference of F contamination of the reactor and (2) that of a normal sample of well-adhered plasma polymer layers without primer. (The XPS data for (2) were available before the incident occurred.) The interface between the first plasma polymer and the substrate metal can be reached only by sputtering the plasma polymers. The two arrows in Fig. 16 indicate the location of the interface in the cross-sectional profiles. The TMS plasma polymer/substrate interface of the failed sample shows a significantly lower Si/C ratio (0.2–0.3) than that of the normal sample (0.9).

This situation clearly demonstrates how F-contamination of the reactor walls can interfere with the plasma polymerization of TMS. These findings indicated the following trends for F-containing gas and solid materials:

(1) F in organic solids is plasma labile due to the high electro-negativity of the F atom and easily comes off into the plasma phase. This is contrary to the widely spread belief that the C–F bond is stable against a plasma because the C–F bond energy is higher than the C–H bond energy.

(2) F in a plasma phase is chemically reactive and reacts with organic surfaces, which are exposed to the F-containing plasma (fluorination of surface).

(3) These two processes create a vicious cycle and the F atom tends to stay in the vicious cycle. The final outcome depends on how long or how many times the vicious cycle repeats.

(4) When F is incorporated into an inorganic structure, it becomes plasma insensitive and escapes from the vicious cycle.

4. From the viewpoint of wire aging in detectors

In the preceding sections, the material deposition from a plasma phase was examined from the viewpoints of surface modifications and nano-film coatings, which are completely opposite to the viewpoints of wire aging in detectors. It is important to recognize, however, that we are looking at the same phenomena from two different sides. Based on what we know from plasma polymerization, the following potentially important aspects for prevention of "aging effects" could be extracted.

The CAP principle seems to be a key to comprehend the very complicated net results recognized as "aging". Ablation could occur by

physical etching or by chemical etching. Physical etching mainly occurs in the sputtering of cathode material, however, the sputtered material could deposit elsewhere in the system including on the anode wire surface. Chemical etching is due to the chemical reaction of reactive species created in the plasma phase near the anode wire. These ablations do not form the deposition of materials on the anode surface, but could damage the integrity of the detection wire.

It is imperative to recognize that organic vapors undergo fragmentation of the original molecules by electron-impact dissociation. What kinds of chemical species will be created as the consequence of the electron-impact dissociation determines the balance between ablation and polymerization, but the impact on "aging effects" is not as simple as polymerization or ablation. For instance, if HF is created in a discharge of CF_4, which is a typical etching gas and reluctant to polymerize by itself but effectively etches Si-based material, it could polymerize and cause the deposition of material. At the same time, HF could chemically attack HF-soluble materials existing in the system.

Polymeric deposits formed by plasma polymerization require backbone-forming elements. In all practical purposes, Si and C could be considered for the backbone-forming elements. Mono-valence elements such as H and halogens reside as side or terminal elements.

Si-containing organic compounds are quite volatile compared to the corresponding molecules without Si and of similar molecular weight. This trend is utilized to increase the vapor pressure of organic compounds by "siliration" (incorporation of Si containing moieties) for gas chromatograph analyses. In the plasma phase, Si has much higher tendency to form polymeric structures and deposits as mentioned earlier. Because of high volatility and high specific polymerization rate, all Si-containing materials should be avoided in the detector system.

Mono-atomic gas, such as He, Ar, Ne, and simple diatomic molecules, such as H_2, O_2, N_2, do not form plasma polymers, and hence no material deposition based on these elements occurs. All hydrocarbons, including the simplest CH_4, polymerize. If hydrocarbons are used, it is necessary to add another gas that inhibits the plasma polymer-ization of hydrocarbons. A small amount of O_2 effectively inhibits the polymerization. CO_2 also could be used for this purpose, but in a less effective manner.

The inhibition of plasma polymerization could be achieved by using oxygen-containing organic compounds such as alcohols, ethers, and ketones. It is anticipated that the smaller the size of the organic ligands, the greater the inhibition effect. It is also anticipated that the inhibition effect would follow a rough trend of alcohol < ethers < ketones, if the sizes of the organic ligands are comparable.

Perfluorocarbons are more reluctant to poly-merize compared to their hydrocarbon counter-parts. However, they should not be used based on the false assumption that perfluorocarbons do not polymerize. C_1- and C_2-perfluorocarbons are typical etching gases used in the microelectronics industry to etch silicon, and are very reluctant to polymerize under normal conditions. However, as mentioned in the discussion of the CAP principle, they can polymerize depending on the discharge conditions and on inadvertent addition of H_2 gas, which could be liberated from many materials used in the system. It should be noted that these gases are very effective etching gas in plasma etching of Si, but not effective etching gas for other materials such as organic polymers.

As the ratio of F/C decreases, perfluorocarbons polymerize readily, and an inclusion of certain chemical structures causes very rapid polymeriza-tion in plasma. For instance, perfluorobenzene (C_6F_6) and hydrofluorocarbons such as $C_2H_2F_4$ polymerize very fast.

Based on these considerations, CF_4 is viewed as a very difficult gas to control with respect to the aging effect. Promising candidate gas mixtures might be found in combinations of inert gases, O_2, CO_2, and low molecular weight alcohol, ethers and ketones.

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