Preparation of Amorphous Carbon Nanofilm by Magneto-Luminous Polymerization

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ABSTRACT: The method and mechanisms to convert methane in gas phase into nanofilm of amorphous carbon; a unique method described as "magneto-luminous polymerization, and characteristic features of such films, with particular emphasis on biocompatibility imparting onto conventional materials, are described. The first key issue is the dissociation of methane in a mode of electrical discharge under the influence of magnetic field to create "magneto-luminous" gas phase in which the deposition of amorphous carbon nanofilm occurs. The amorphous carbon nanofilms (10–30 nm) have unique feature that the carbon film has no chemical functional group, which could cause various forms of interfacial interactions with surrounding medium, particularly with biological systems. Such a nanofilm could provide a great potential of imparting biocompatibility to various (metallic, ceramic, and polymeric) functional implants. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 2636–2645, 2012

Key words: plasma polymerization; interface; biocompatibility; nanofilm; polymerization mechanism

INTRODUCTION

Magneto-luminous polymerization (MLP) is a spin out of "plasma polymerization" which refers to the process that yields organic thin film deposition from organic molecules in low-pressure gas phase by means of electrical discharge. MLP is a unique mode of plasma polymerization that distinguishes itself from the rest of plasma polymerization.

The term plasma polymerization has been used since the first "glow film" was reported in 1960.[1] However, there is no clear definition of terminology, and seemingly the same process has been expressed by various terminologies based on preference and perception of the process by researchers working with the process; e.g., plasma-enhanced chemical vapor deposition (PECVD), plasma-assisted chemical vapor deposition (PACVD), plasma chemical vapor deposition (PCVD), and luminous chemical vapor deposition (LCVD), which has been used synonymously with plasma polymerization by the author of this article. These somewhat confusing situations are mainly due to the complexity of process itself, and conversely, the lack of understanding of fundamental reaction mechanisms of "plasma polymerization" by practitioners of the process.

The term "plasma" to describe the gas phase created by electrical discharge was coined by Langmuir in 1928,[2] while the "plasma" had been used in different meanings in different domains of natural science. Why he chose "plasma" was not clear.[3] The ambiguity of term "plasma" is the main cause of the confusion. The term "polymerization" also has some arguable ambiguities. In the broadest context, when a solid organic material is formed from small molecules in gas phase, it should be described that the gas molecule (with small mass) polymerized to a polymer (with large mass), even though the mechanism how it happened is not known. However, some polymer scientists today tend to insist to the narrow view that the polymerization mechanism should be known to be called as polymerization.

It is an interesting irony in the history of polymer science, because when the term "polymer" was first proposed by Staudinger in 1926,[4] nobody paid serious attention to the concept of "polymer," and Staudinger had to work seven additional years to convince others using naturally occurring cellulose derivatives, without knowing mechanism by that cellulose had been polymerized.

These ambiguities in "plasma" and "polymerization" undoubtedly play key roles to use various terms described above, mainly describing the process used and properties of the product. However, there is a common denominator in those processes; the use of electrical discharge of gas, which is recognized as glow discharge because the gas phase

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become luminous or glowing gas phase. To create an electrical discharge, dielectric breakdown of gas phase, which convert dielectric gas phase to electrically conducting gas phase, must be caused.

The dielectric breakdown of gas phase in low-pressure has been examined mainly with mono-atomic gas such as argon in DC discharge, according to the Townsend/Paschen approach based on hypothesis of ionization of gas by the secondary electron emitting from the cathode surface.[5,6] This trend is obvious, because there was no need to consider the gas phase breakdown of molecular gas until the plasma polymerization that utilized electrical discharge of molecular gases was developed in late 1950's.

At the dawn of plasma polymerization as an intriguing technology to lay down a thin film on a substrate, it was simply assumed that the investigation of breakdown voltage investigated with mono-atomic gas in DC discharge also apply to the breakdown of molecular gases used for plasma polymerization by RF discharge, in which discharge voltage, V, cannot be measured and only power $W = V \times I$, (I is current), is the controllable parameter.

MLP is a unique mode of plasma polymerization, which utilizes the interaction of electrons in the electric field and of electrons in the magnetic field with organic molecules in gas phase. The method could be described by "magnetron plasma polymerization," because the process uses electrode equipped with a magnetic enhancement, which is generally termed as magnetron. However, this term is intentionally avoided in this article because the magnetron has been used mainly in sputter coating of target material (mostly a metal used as the cathode of DC discharge), and the fear for possible contamination of plasma polymer with cathode metal might shy away some potential users of magnetron plasma polymerization. Examination of kinetic of magnetron plasma polymerization and of magnetron sputter coating revealed that the principles of magnetron plasma polymerization and of magnetron sputter coating are significantly different,[7] which could be expressed by the difference of the ionization of gas used and the dissociation of (molecular) gas used in respective processes, according to key issue described in this article.

In light of recent investigations of dielectric gas phase breakdown of molecular gases,[8] the very unique advantages of MLP became clearer as described in this article. Furthermore, the term MLP is used avoiding the term "Plasma," which has been used in the context that plasma is ionized gas created by the ionization of gas. The electrically broken down gas phase of organic molecule can be described more adequately by "luminous gas phase" in which the major species are neutral photon-emitting excited species that can be polymerized, while ions formed in gas phase cannot be polymerized.

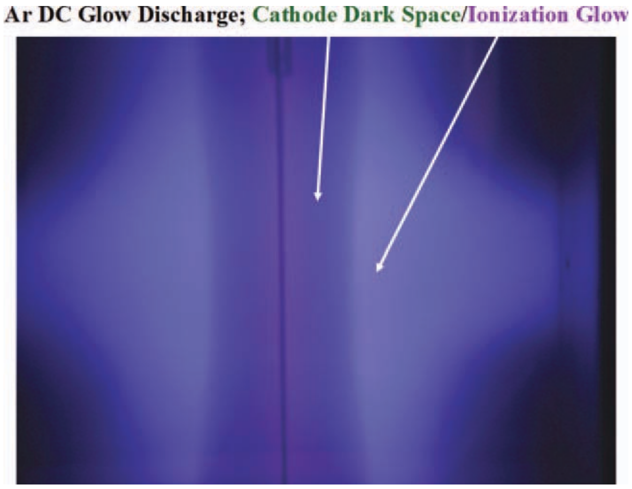


Figure 1 The glow develops at the onset of gas phase breakdown with Ar. Ionization glow is separated from the cathode surface by the dark space (cathode fall). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

GAS PHASE BREAKDOWN OF ORGANIC MOLECULES

Dielectric gas phase breakdown of organic molecules in dc discharge

The fact that the mechanisms of gas phase breakdown of molecular gases is significantly different from that of mono-atomic gases was discovered only recently (2003). It was the discovery of "dissociation glow" that made possible to distinguish the two mechanisms, in DC discharge of deposition molecular gas such as methane and trimethylsilane (TMS),[9–12] in contrast to "ionization glow" that is the only glow develops with mono-atomic gases. The convincing evidence that the mechanisms of gas phase breakdown for mono-atomic gases and for organic molecules are different is seen in the pictures of glows develop at the onset of glows. Figure 1 depicts the glow of argon, and Figure 2 shows the glow of TMS observed with the same experimental setups, which use a metal plate cathode, placed in the middle, paired with two identical magnetron anodes. The magnetron anodes are used to observe the shaping of the negative glow near the anode, and the key characteristic feature of the glow near the cathode is not influenced by presence or absence of magnetic field on anodes. With an organic molecule (TMS) the first glow develops is the dissociation glow appears as the cathode glow; i.e., the glow touches the cathode surface and there is no dark space, in which electrons are supposed to be accelerated by the electric field and gain sufficient energy to ionize the gas to cause gas phase breakdown, according to the ionization concept of gas phase breakdown.

It was also found previously that the main controlling factor of DC cathodic plasma polymerization

Figure 2 The glow develops at the onset of gas phase breakdown of TMS. The main glow is the dissociation glow of trimethylsilane touching to the cathode surface; i.e., there is no cathode dark space. The second glow (ionization glow), which develops subsequent to the dissociation glow, is separated from the cathode surface as well as from the dissociation glow by the cathode fall. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

is the discharge current density near the cathode, not the discharge voltage,[13,14] which intensifies the importance of recognizing the fundamental difference in the gas phase breakdown steps for a mono-atomic gas and for an organic molecules.

The conventional gas phase breakdown mechanism postulated by the breakdown of mono-atomic gas was based on the concept that ionization of gas under the applied voltage. The electrons emanating from the cathode surface are accelerated in the dark space in between the cathode surface and the edge of glow to gain enough energy to ionize the gas. The striking difference between Ar discharge in Figure 1, and TMS discharge in Figure 2, is the absence of the dark space (cathode fall region) in TMS discharge, which not only indicates that the ionization principle of gas phase breakdown does not apply to the gas phase breakdown of organic molecules but also cast doubt on the validity of the ionization concept of gas phase breakdown for the gas phase breakdown of mono-atomic gas in DC discharge.

Gas phase breakdown investigated by breakdown current and voltage in DC discharge

According to the classical interpretation, the gas phase breakdown has been treated as ionization process, and accordingly only the breakdown voltage has been examined to describe the dielectric breakdown of gas phase. Alternatively, the dielectric breakdown of gas phase, in general, could be viewed as the electron-impact excitation of gas to create excited species (inclusive of ions), in which excited species function as the energy transferring medium. The dissociation of molecules means that ionization of molecules does not occur, and ions created subsequently are ions of H_2, the main ionizable dissociation product of the original molecule.[11]

The concept of luminous gas phase or low-temperature plasma phase as an energy transporting medium could be explained by an analogy in how the energy of *tsunami* is transferred by water; i.e., water act as the energy transferring medium, while water is not being transported except near the shore. Similarly, neutral excited species are not moving from cathode to anode, but electrons are moving faster to the anode because of higher electric conductivity of luminous gas phase. The efficiency of energy transferring medium could be judged by the conductivity of the broken-down gas phase that requires the values of breakdown voltage and break-down current, which are measurable parameters in DC discharge, but not in RF discharge that has been mainly used for “plasma polymerization.”

Any electron-impact reaction beyond ionization of mono-atomic gas such as Ar depends on the type or nature of gas. Hence, the investigations of dielectric breakdown of gases as function of the type of gas; mono-atomic gas such as Ar; simple molecular gas such as N_2 and O_2; and dissociable organic molecules such as CH_4, are necessary. Since mono-atomic gas Ar has no capability of participating or causing chemical reaction, it is easy to diagnose the broken-down gas phase; however, the results and interpretation cannot and should not be extended to molecular gases. With molecular gas; e.g., O_2, N_2, CH_4 etc., the electron-impact dissociation and excitation of molecule in gas phase becomes the predominantly important factor in the breakdown of gas phase. The major constituent species in the broken-down gas phase are excited neutrals; i.e., neutral species outnumber ions in order 10^6,[15] which defies the concept of ionized gas.

The breakdown process should be investigated recording both breakdown voltage, V_b, and breakdown current, I_b. The results could be presented in terms of all derivable parameters from V_b and I_b, such as; energy $W_b = V_b \times I_b$, conductivity $= I_b/V_b$, and input energy per mass $= W_b/F^*M$, where F is volume or molar flow rate, M molecular weight of gas. Numerous plots made using those parameters against the system pressure revealed the following important trends: (1) The influence of type of gas; i.e., mono-atomic gas Ar, molecular gas with low electron negativity N_2, molecular gas with high electro negativity O_2, and organic molecule CH4, on the breakdown voltage is rather marginable, but influence on discharge current, which has not been measured in conventional studies, are significantly

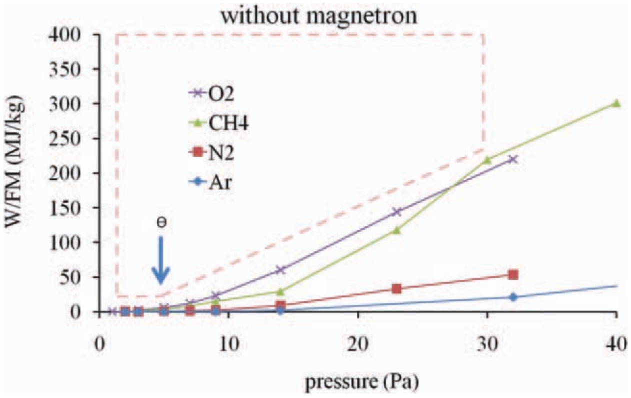


Figure 3 Gas phase breakdown phenomena expressed by the plots of breakdown power, *W/FM* in MJ/kg against system pressure. Gas phase breakdown occurs only in the domain above the threshold pressure θ. The zone shown by red line is the domain in which gas phase breakdown cannot occur. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

greater. (2) Consequently, the plots of those parameters against the system pressure showed nearly identical trend, because V_b is nearly constant in comparison with the variation of I_b. In contrast to the breakdown voltage, the breakdown current showed great dependency on the type of gas.

Since the only controllable experimental parameter of RF discharge is the wattage, the following discharge characteristics are presented by the plot of the discharge energy per mass (J/kg), which is given by *W/FM*, where *W* is discharge wattage, *F* is molar flow rate, and *M* is the molecular weight of gas used. The parameter, *W/FM* is the key parameter that control plasma polymerization by RF discharge.[9,16] The use of this parameter is particularly important dealing with organic molecules because gas is consumed by polymerization and deposition. Dealing with non-consumable gases, the system pressure is a simple parameter that is controlled by the number of gas in the system regardless of a closed or flow system. However, with consumable gas, organic molecules, the pressure is dependent on the flow rate and the consumption rate, and the use of *W/FM* parameter (J/kg) is necessary.

Figure 3 depicts the general trends found with plots of *W/FM* as a function of pressure for Ar, N_2, O_2, and CH_4. The plots tell us what we could extract from the breakdown phenomena as a function of pressure:

1. Plots for the four gases representing mono-atomic (non-deposition, non-dissociable) gas, Ar; dissociable but non-deposition molecular gas, N_2 and O_2, and deposition molecular gas, CH_4, are by and large the same in low-pressure domain below the transition pressure shown by Θ_p.
2. Ar, which has been main topic of breakdown phenomena in conventional studies, is the least dependent on pressure among gases investigated.
3. There are clearly identifiable two domains of breakdown gas phase separated by the transition point pressure, Θ_p.
4. The transition point pressure, Θ_p is nearly independent of type of gas.

Gas phase breakdown under the influence of magnetic field

Figure 4 shows the dependence of breakdown phenomena on the system pressure under the influence of magnetic field expressed by the identical parameter used in Figure 3. The change of breakdown phenomena due to the influence of magnetic field can be best visualized by comparing the phase diagram of gas phase breakdown with and without magnetic field; comparison of Figures 3 and 4.

Figure 4 shows the shift of phase diagram, based on the dependence of energy transfer capability of the broken-down gas phase on system pressure. It is important to note that the parameter used for Y-axis; i.e., *W/FM* is a measurable parameter in RF discharge. The presence of magnetic field on the cathode changes the characters of luminous gas phase completely. The shift of the phase diagram due to the influence of magnetic field for each gas is clearly seen; i.e., very high energy transfer occurs at very low-pressure with all gases examined, where the energy transfer hardly occurs without magnetic field. The pressure dependence show there are two groups of gases; one that show the remnant of the transition point pressure (Ar and N_2) and another

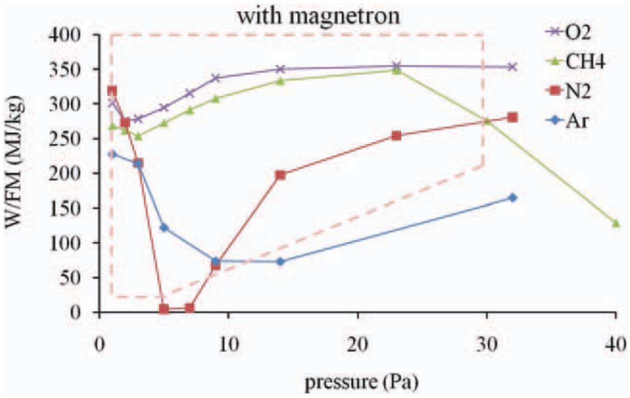


Figure 4 Gas phase breakdown under the influence of super imposed magnetic field on the cathode (magnetron). The domain of gas phase breakdown shifts to the no-discharge zone observed without magnetic field. Very high current discharge occurs in very low pressure, below the threshold pressure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that maintain high energy transfer nearly independent of pressure (O_2 and CH_4).

Important aspects of the influence of magnetic field on the dielectric breakdown of gas phase consisting with deposition gas (CH_4) are the following:

1. The phase diagram of gas phase breakdown with magnetic field is totally different from that without magnetic field. There is only one domain for magnetron discharge in all practical sense, which is located in the domain where no gas phase breakdown occurs without magnetic field.
2. The sharp increase of breakdown voltage with decreasing pressure observed without magnetic field, in the low pressure below the transition point pressure, virtually disappears and the very high current is created by very low applied voltage at the lowest pressure.
3. With magnetic field, very high currents (over 50 mA) flow through the luminous gas phase in pressure range below the transition point pressure observed, where breakdown currents are <1 mA without magnetic field. These very high currents are caused by the lowest breakdown voltage observed (The ceiling values seen in the plots are due to the ceiling current set for the power supply used.).
4. The main domain of MLP is the low pressure range, which is below the transition point pressure observed without magnetic field.

The most significant but mysterious fact reveled by examination of the dielectric breakdown of gas phase under the influence of magnetic field is the very high current derived by very low applied voltage at very low-pressure domain. The discharge current observed in the low-pressure domain is at least an order of magnitude greater than what have been observed without magnetic field using the same reactor, gas and same set of operation parameters. All those surprising findings are not beyond our comprehension of the gas phase breakdown process; if we recognize that the luminous gas phase created is not ionized gas but gas phase consisting of highly electrically conductive radiant matters. The big question remains, however, is how such a high current could be created by very low applied voltage?

ELECTRON-IMPACT DISSOCIATION OF GAS MOLECULES AND LUMINOUS POLYMERIZATION MECHANISM

Nearly all polymers formed by luminous polymerization contains large amount of free radicals detectable by electron spin resonance (ESR), and there is no doubt that polymer formation proceeds with free radicals. However, the presence of large number of free radical in deposition is in contradiction with the conventional free radical polymerization mechanism; i.e., polymers formed by conventional free radical addition–polymerization do not contain sizable free radicals because the recombination of two growing molecules with free radical at the growing chain-end is the termination process of free radical polymerization. Furthermore, organic molecules that are not monomers of free radical polymerization; e.g., saturated vinyl monomers, form polymers just as easily as corresponding vinyl monomer in the luminous gas phase. In luminous polymerization, reactive species with free radical(s) are created by the electron-impact dissociation of molecules, and many gases used in plasma polymerization; e.g., methane, benzene etc, do not have functional groups for free radical addition–polymerization, polymerize nearly as easily as functional group containing molecules (monomers of free radical polymerization). In other words, the evidence that luminous polymerized polymers contain large amount of free radicals is the proof that the free radical luminous polymerization is not conventional chain growth free radical polymerization.

In conventional free radical polymerization, the monomer must have a chain carrying functional group; e.g., double bond, or triple bond, and a small concentration of free radical forming initiator; e.g., peroxide, is added to a reaction mixture. The concentration of the initiator determines the molecular weight of resultant polymers; i.e., the greater the concentration of initiator, the kinetic path length is shorter and polymers with lower degree of polymerization are formed; i.e., the initiation and the termination are coupled. In luminous polymerization, no initiating chemical is added in the polymerization system, and no particular functional group for chain growth polymerization is necessary. The chemically reactive species to form polymers are created by the electron-impact dissociation of molecules.

The electron-impact dissociation of molecules (breaking of any covalent bond including π bond) yield free radicals, but those free radicals mainly recombine each other, which is the termination step of conventional free radical polymerization, because so many free radicals are formed within a short time span, the kinetic path length is zero; i.e., no polymerization by conventional free radical addition–polymerization mechanism. This situation is analogous to the case that too much initiator is added to the free radical polymerization system; i.e., no polymer formation because the growing chains recombine with abundantly available growing molecules with free radical end before enough addition of monomer molecules occur yielding formation of many low molecular oligomers.

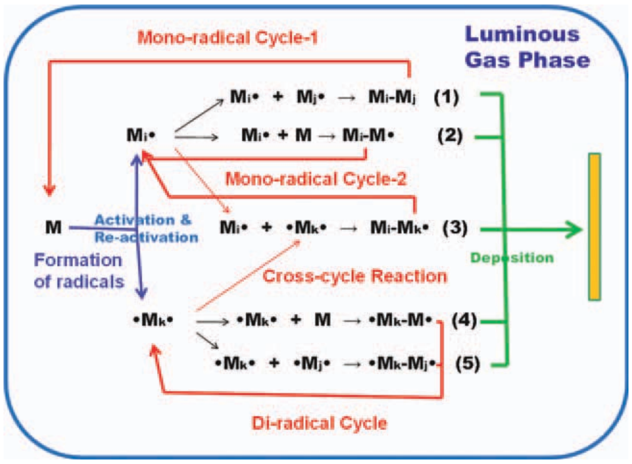


Figure 5 Schematic representation of polymer formation mechanism in luminous gas phase: Repeating step growth polymerization mechanism. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The luminous polymerization proceeds via repeated recombination of free radicals and re-excitation, which means the recombined species, are subjected to reactivation (formation of free radicals) to form free radicals on the once recombined molecules. The dissociation of molecules, including the products of recombination of free radicals and molecular species with a free radical, occurs by the electron-impact dissociation in the luminous gas phase. The complex polymer formation mechanisms are expressed by the Repeating Step Growth Polymerization or rapid step growth polymerization (RSGP) mechanism, because the molecular weight increase occurs step wise, but in rapid repeating mode.[16] The overall mechanisms of polymer formation and deposition are schematically depicted in Figure 5 in a revised format that includes deposition steps. Important features shown in Figure 5 are the following:

1. The formation of free radical and recombination of free radicals occurs independently; i.e., these two kinds of reactions are not coupled. Under large free radical formation rate, the recombination cannot catch up with the formation rate, which leads to a large number of unreacted free radical left in the deposition (plasma polymer) and leave un-reacted free radicals in plasma polymerization products.
2. The initiation reaction that is the first step chemical reaction, without which the whole process does not proceed, and the deposition steps that bring down species in the polymer formation steps in the luminous gas phase to the substrate surface are not coupled either. Any species described in reaction (1) through reaction (5) could deposit on substrate surface and on any other surfaces that contact with the gas phase.
3. The deposition of any species in luminous gas phase occurs when the specie fails to bounce back upon colliding with a surface, which also means that not all deposition of species could be chemically bonded to the surface. The collision of a free radical bearing species with surface has higher probability of forming chemical bonds with the substrate material.

Because of these features that are built in the luminous polymer formation mechanisms, plasma polymerization, in general, is highly system dependent. Accordingly, a generic plasma polymerization of styrene or any other molecule cannot be defined. In other words, various kinds of plasma polymers could be prepared from a monomer, e.g., acrylic acid, by plasma polymerization.

PRACTICAL MODE OF MAGNETO-LUMINOUS POLYMERIZATION

Coating of amorphous carbon nanofilm by magneto-luminous polymerization

Magneto luminous gas phase is created by superimposing magnetic field on the cathode consisting of non-magnetic metal. For coating of nanofilm, audio frequency (e.g., 50 kHz) discharge rather than DC discharge is used for a practical reason to create uniform coating on both sides of a substrate. Audio frequency discharge is essentially alternating polarity DC discharge, and all unique features of DC discharge are retained. Although numerous ways of coupling the magnetic field to the cathode could be used, the simplest coupling of magnetic field to the cathode has been used in MLP in laboratory reactors, which can be also used in industrial scale operation with minor modification to accommodate the change of mode of operational conditions for the final coated products. In the industrial scale continuous operation, substrates must be transferred by linear (vertical or horizontal) motion.

Figure 6 is a pictorial view of magnets assembly; a central circular iron plate and a circular iron plate ring are bridged by eight bar magnets maintaining the same polarity of all bar magnets. The center circular plate become one magnetic pole; e.g., the south pole, and the circular ring plate become the opposite magnetic pole; i.e., the north pole. This assembly is attached to the back side of an electrode (the front side is facing to the counter electrode having the identical magnetic field assembly), and an audio frequency power is applied to the both electrodes. To maintain the symmetry of luminous gas phase, the symmetrical power supply; a power supply with floating power outlets, is used. Without magnetic field, the cathode glow develops, on both electrodes,

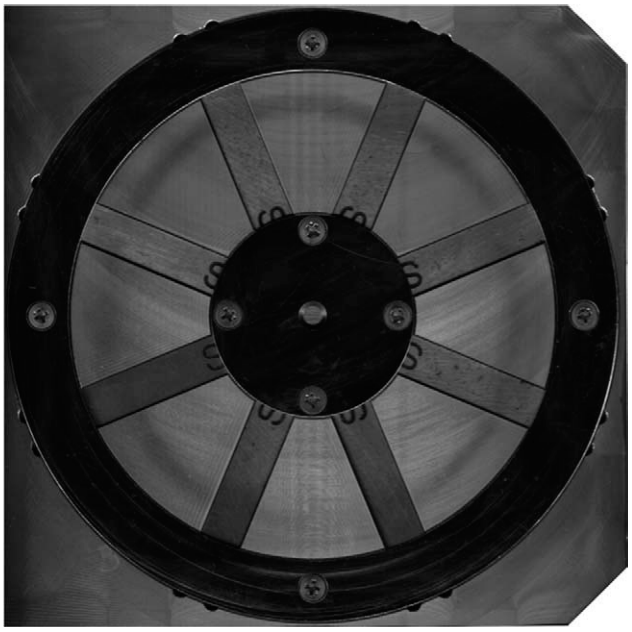


Figure 6 Pictorial view of magnetic field arrangement; the center iron plate become the south pole, and the outer circular ring iron plate becomes the north pole of the circular planar magnet, which will be placed behind an titanium plate electrode.

covering the entire surface of an electrode. With magnetic field, the glow develops near the electrode surface (toroidal glow) is completely different as shown in Figure 7. The toroidal glow does not touch the electrode; i.e., the toroidal glow is floating in the gas phase.

The electrode surface below the toroidal glow (toroidal glow surface) has no deposition of material under properly selected operational conditions, while the remaining electrode surface receive varying degree of deposition and of characteristics. Since the toroidal glow surface remains deposition free, MLP can be operated continuously for extended period of time; e.g., continuous operation for a month, with continuous feeding of substrates and gas. The characteristics of the coating do not change in the entire span of one month's continuous coating operation. This is a very unique feature of MLP, which cannot be achieved by other mode of low-pressure plasma deposition processes because of the deposition on electrodes (energy input surface), which makes a continuous industrial application virtually impossible.

In most cases, small amount of oxygen is added to the feeding gas. The main objectives of adding oxygen are (1) enhancing the deposition free "toroidal glow surface," and (2) slowing down deposition rate by consuming carbon atoms produced by the dissociation of methane and removing from the vacuum system. It is not intended to make the surface of film hydrophilic. Without feeding O_2, the surface of nanofilm is moderately hydrophilic, because the trapped free radicals on the top surface of nanofilm react with oxygen when coated substrates are taken out of the vacuum reactor. The O contents by XPS of coatings with and without O_2 feed are essentially the same. Amphoteric hydrophilicity/hydrophobicity seems to be one of key requirements for biocompatibility by "minimum perturbation principle" since no pure water exists in any biological system and hydrophobic components exist in most biological systems. To make surface highly hydrophilic to improve, biocompatibility of polymer surface is a misleading concept.

The gas phase in between two toroidal glows are filled with less intense but more uniform luminous gas phase (with respect to the toroidal glow), which is the main luminous gas phase of alternating magneto DC discharge. The substrates to be coated are placed in the middle portion of two electrodes by means of rotating sample holder, and the substrates move in and out of the luminous gas phase. The movement of substrate yields very uniform coating on both side of a substrate.

The following general advantages of using MLP have been known.[7]

1. Confinement of glow volume to inter electrode volume, which increases the yield of polymer deposition on substrate under the same flow rate and reduces the wall contamination of reactor. Substrates move through the luminous gas phase.

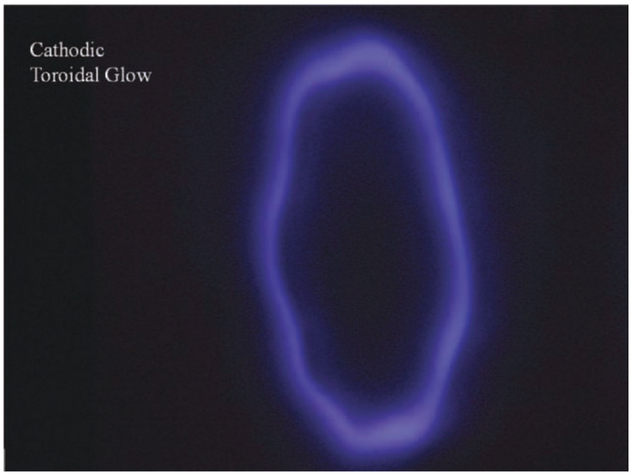


Figure 7 Pictorial view of the toroidal glow develops by a magnetic field enhanced electrode by audio frequency discharge. The toroidal glow develops near the surface where the magnetic field line is parallel to the electrode surface. The glow develops only in the toroidal glow and the remaining surface of electrode is not participating with the creation of luminous gas phase. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

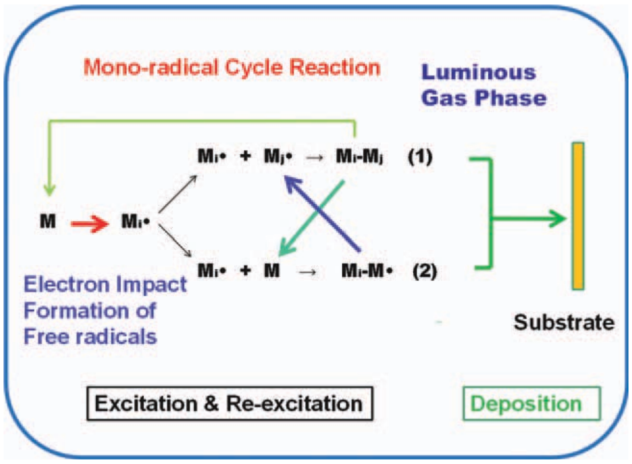


Figure 8 Repeating step growth polymerization mechanism for simple molecules without functional group that could create di-radicals by electron-impact dissociation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

2. The polymer deposition does not occur onto the electrode surface below the toroidal glow. Consequently, a steady state plasma polymerization is established within a short induction period and remain for a long period of operation; e.g., continuous operation for a month.
3. Sputter coating of cathode material does not occur under the preferred conditions for plasma polymerization; however, sputter coating can be achieved by the same reactor under the different conditions that favor sputter coating, i.e., selection of metal, pressure, type of gas, discharge voltage.
4. Better adhesion of nanofilm with uniform deposition thickness than most other modes of plasma polymerization can be obtained.

The continuous operation capability described above is probably the most significant feature of MLP in practical industrial scale applications, which distinguish the method out of other modes of plasma polymerization.[17] Further details of MLP of methane are described below.

Advantages of using simple molecular gas, e.g., CH_4, in magneto-luminous polymerization

Obvious advantage of using simplest gas in a series, such as CH_4 is the simplicity of polymerization mechanism; in absence of functional groups that cause formation of di-radicals by electron-impact reactions. Figure 8 schematically depicts the two important factors in the simplified reaction mechanism; i.e., excitation and re-excitation reactions on the left side and deposition of species from luminous gas phase on the right side. These two processes are not coupled but the dominant process is greatly influenced by the system pressure, because the ratio of gas–gas collisions/gas–surface collision increases with the system pressure in practical large enough reactors.

The excitation and re-excitation cycle shown on the left side determine the kinetic path length, which determines the size of reactive species that deposit by gas–surface collisions. This scheme is schematically depicted in Figure 9. The kinetic path length increases with system pressure and cause deposition of larger reactive species. As the size of depositing species increases, the packing density of deposition decrease and the contact area per mass also decreases, which lead to the decreased adhesion strength and the less tight nanofilm. Since the simplified polymerization mechanism for simple (no functional group containing) gas depicted in Figure 8 is still RSGP mechanism; i.e., no long chain formation, the model with spherical species seems to be quite adequate to describe the balance between the reaction path length and deposition. The most significant advantage of magneto plasma polymerization is in the balance of these two factors. Since MLP occurs in low-pressure below the transition point pressure (without magnetic field), it is possible to get very tight nanofilm with good adhesion to the substrate.

Unique interfacial behavior of magneto-luminous polymerized CH_4 nanofilm

The magneto-plasma polymerization of CH_4 yields a nanofilm that can be described as amorphous CH_x with surface CH_xO_y. The surface oxygen is incorporated by the reaction of trapped free radicals in the

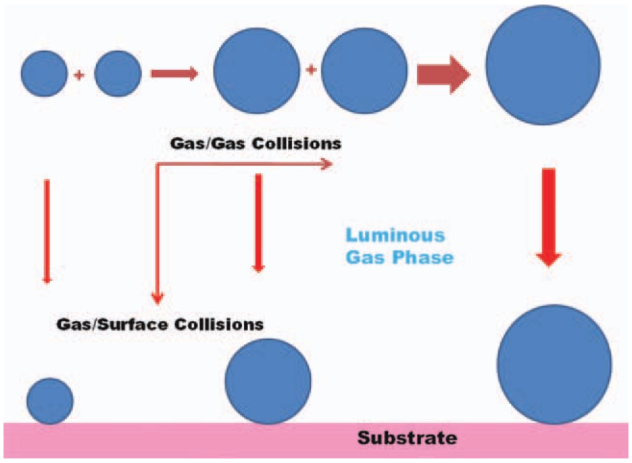


Figure 9 Balance of gas–gas collisions, which determine the kinetic path length, and gas–surface collisions, which determine the deposition of reactive species. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

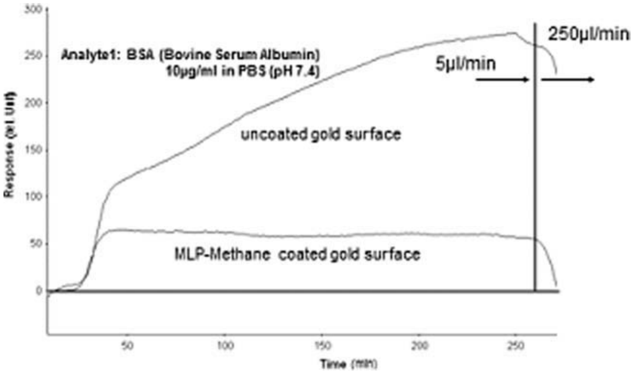


Figure 10 Time dependent adsorption of protein, bovine serum albumin, in a simultaneous parallel adsorption measurement setup from 10 μg/mL PBS (pH 7.4) standard phosphate buffer solutions, at a flow rate of 50 μL/min: (A) uncoated gold surface (standard reference), and (B) MLP-CH_4 coated reference surface; the experiment was stopped after 250 min. To wash the whole systems, the flow rate was increased to 250 μL/min.

amorphous carbon nanofilm with ambient oxygen molecules when coated substrate is taken out of the reactor; oxygen is the best scavenger of free radical within the system environment. Although a certain amount of oxygen or air is intentionally introduced in the polymerization system, it is not intended to make surface hydrophilic as described before. In luminous polymerization system, the gas phase O_2 does not incorporate into polymer deposition, which is described by "in/out rule" in plasma polymerization.[16]

The important feature of the amorphous carbon nanofilm is the imperturbability of the surface-state of the nanofilm coated material. The surface-state is the top surface layer, roughly up to 30–40 nm of material, which is significantly different from the bulk state of the same material. MLP of CH_4 is actually the implantation of new surface-state on the substrate material.

The interfacial interaction of film surface with contacting medium, including biological system, occurs by mutual finding of strong interaction (positive or negative) by rearrangement of interactive chemical moieties on both surface and contacting medium,[9,18] which is not a spontaneous passive deposition of biological elements on the surface. According to this principle, the magneto-luminous polymerized CH_4 coated material with imperturbable surface-state causes the minimum or no interaction with biological system.

This situation can be clearly seen in the dynamic adsorption experiments shown in Figures 10 and 11.[19] In these figures, adsorption kinetics are compared simultaneously in parallel flow systems with the reference gold surface, which is provided by the instrument maker, and magneto-plasma polymerization of CH_4 coated on the reference gold surface.

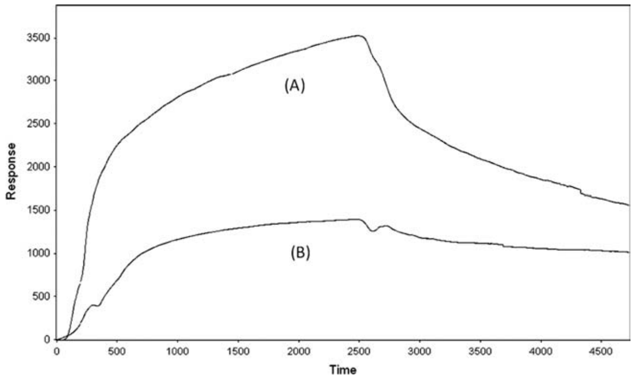
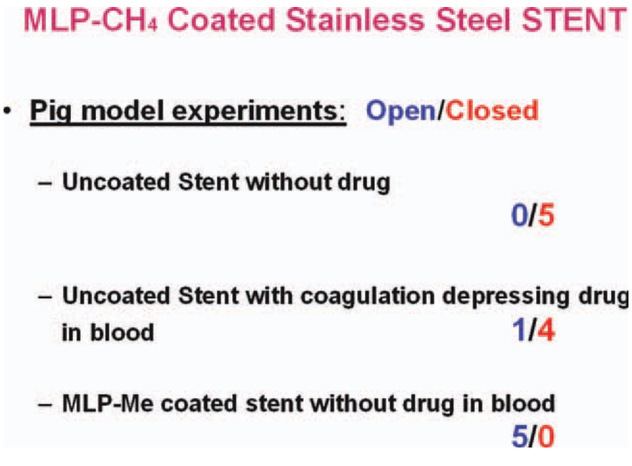


Figure 11 Time dependent unspecific bacterial adsorption was measured in a simultaneous parallel adsorption measurement setup with 1 × 10^8 *Enteroccocus faecalis* in LB-media with a flow rate of 50 μL/min; (A) uncoated gold surface (standard reference), and (B) MLP-CH_4 coated reference surface; the experiment was stopped after 250 min but, in this case the flow rate was not increased for washing of surfaces.

The details of such adsorption study are interesting and important research subject by itself, but in this study only the relative comparisons are attempted to identify the effect of the imperturbable surface-state created by magneto-plasma polymerization. The data obtained are sufficient for this purpose.

Adsorption of protein and bacteria on the surface of magneto-luminous polymerized amorphous carbon nanofilm are significantly lower than those on gold surface. Furthermore, adsorption on gold surface as well as on magneto-plasma polymerized surface is reversible; i.e., adsorbed materials do not adhere to the surface (The flow rate of washing cycle in Figure 11 was the same as the adsorption cycle, and the de-adsorption rate is much slower than the case shown in Figure 10).

These results indicate that the amorphous carbon nanofilm causes significantly less interfacial



MLP-CH₄ Coated Stainless Steel STENT

- **Pig model experiments:** Open/Closed
  - Uncoated Stent without drug 0/5
  - Uncoated Stent with coagulation depressing drug in blood 1/4
  - MLP-Me coated stent without drug in blood 5/0

Figure 12 Summary of *in vivo* blood coagulation tests (Pig model). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

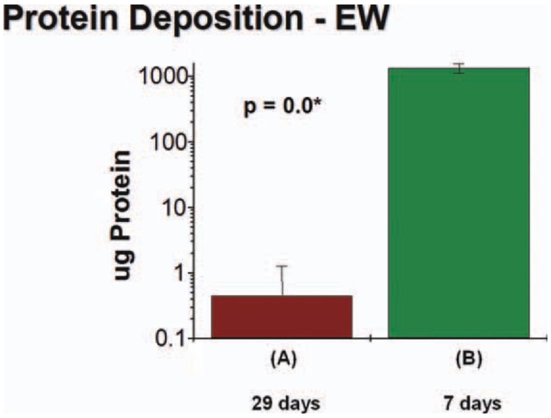


Figure 13 Comparison of protein adsorption by (A) MLP-CH_4 coated extended wear contact lens worn for 29 days continuously and (B) similar lens (different brand) coated with other method worn for 7 days continuously. Despite of four times longer period of continuous wearing time, MLP-CH_4 coated lens accumulation of protein is less than three orders of magnitude of Sample B. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

interaction with biological elements than the gold surface, which is the great positive feature in imparting biocompatibility to materials to be used in contact with biological systems. It has been generally observed in preliminary investigations that the best interfacial interaction control was observed the minimum thickness of the coating; e.g., 10–20 nm, and further increase of thickness does not improve imperturbability of surface, which is along the predicted line based on the deposition mechanism described in Figure 9.

Some experimental data also support this assessment; the minimum perturbation to biological system is the key factor for biocompatibility. It should be noted here that ''biocompatibility'' depends on the biological system that is in contact with the artificial surface, and there is no generic biocompatibility one could discuss. However, it is possible to find the general trends by comparing the MLP-CH_4 coated surface with other surfaces, which do not have the coating.

Nanofilm encapsulation of all exposed surfaces of metallic stent showed no closure of stents five out of five cases, while all of uncoated stents were closed by coagulation of blood in pig model[20] as depicted in Figure 12 (The nature of the coating was not disclosed, and the reference quotes as polymer coated stents).

Extended wear contact lens coated with MLP-CH_4 (Sample A) showed three orders of magnitude less adsorption of protein after 29 days of wearing than that of comparable (extended wear) lens (Sample B) with a different surface treatment in one week wearing[21] as shown in Figure 13.

All those data strongly indicate the general trend that the imperturbable surface-state of MLP-CH_4 coated surfaces causing no interaction with surrounding medium and cause no response of biological systems. The interfacial interaction between an artificial surface A and a biological system B could be expressed by the product of the extent of interfacial response of the surface [A] and that of the biological system [B]; i.e., Interfacial Interaction $=$ [A] $\times$ [B]. If the surface A does not cause or respond to interfacial interaction potential, which is the case of MLP-CH_4 surface, the equation changes to Interfacial Interaction $= 0*[B] = 0$, irrespective of the value of [B]. This is the fundamental concept of the minimum perturbation principle of biocompatibility.

The minimum perturbation concept of biocompatibility provides a realistic approach to impart the biocompatibility to artificial materials to be used in contact with biological systems, and the applications of nanofilm coating by MLP of methane have proved an excellent mean to impart biocompatibility to material surfaces in various shapes and sizes to be used in certain biological environments.

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