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Electron dynamics of low-pressure deposition plasma*

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Abstract: When the electric field in the dark gas phase reaches the threshold value, an electron avalanche (breakdown) occurs, which causes dissociation of organic molecules, excitation of chemically reactive molecular gas, and/or ionization of atomic gas, depending on the type of gas involved. The principles that govern these electron-impact reactions are collectively described by the term "electron dynamics". The electron-impact dissociation of organic molecules is the key factor for the deposition plasma. The implications of the interfacial avalanche of the primary electrons on the deposition plasma and also other plasma processes are discussed. The system dependency of low-pressure plasma deposition processes is an extremely important factor that should be reckoned, because the electron dynamic reactions are highly dependent on every aspect of the reaction system. The secondary electron emission from the cathode is a misinterpretation of the interfacial electron avalanche of the primary electrons described in this paper.

Keywords: breakdown process; electron dynamics; primary-electron emission; plasma polymerization; magnetron plasma polymerization.

INTRODUCTION

Plasma polymerization, which is also described by terms such as plasma chemical vapor deposition (PCVD), plasma-assisted chemical vapor deposition (PACVD), plasma-enhanced chemical vapor deposition (PECVD), luminous chemical vapor deposition (LCVD), etc., is unique in that the chemically reactive species necessary for the polymerization is created by the electron-impact dissociation of the starting organic molecules, not by thermal excitation or chemical reaction. The *electron dynamics*, in contrast to the thermodynamics, controls the very initial step of polymerization. Therefore, it is imperative to examine the electron dynamics in the low-pressure plasma processes that occur in weakly to very weakly ionized gas phase.

GAS-PHASE BREAKDOWN PROCESS

According to the widely subscribed mechanism of the gas-phase breakdown [1,2], the primary electrons are created in the gas phase by the impact of naturally occurring ionizing-radiation, such as cosmic rays, and cause the subsequent ionization and bombardment of ions on the cathode surface, which causes the emission of the secondary electrons and ionization of gas. Namely, the primary event of the process is

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considered to be the ionization of gas. This mechanism is based on Townsend's theory with the assumption of the gas-phase ionization, which we do not agree to consider as a fact.

The recent discovery of the cathode glow in the deposition plasma of organic vapor [3–6], which showed that the dissociation of molecules occurs prior to the ionization, defies the above-mentioned classical mechanism. According to our recent findings, the electrons that cause the dielectric breakdown of the gas phase are not the secondary electrons explained by the classical interpretation of the gas-phase breakdown but are the primary (free) electrons pulled out of the surface state of the cathode metal. When the electric field in the dark gas phase reaches the threshold electric field of the dielectric breakdown of the gas phase, the abrupt increase of the electron flux in the order of over 10^6 occurs, which could be best described as the interfacial electron avalanche. The following sections describe an alternative theory of the gas-phase breakdown, which is the very first step of various subsequent steps involved in the deposition plasma. Without understanding the first step, any explanation of the deposition plasma process is deemed to be a groundless speculation.

The classical explanation ignores the fact that the electric field profile changes drastically when the inception of glow discharge occurs. In the dark gas phase, the voltage profile is a straight line, and the electric field, E, is generally given by V/d, where V is applied voltage and d the distance between cathode and anode. The increase of applied voltage increases the electric field in the dark gas phase but does not increase the dark current. When the threshold electric field, above which the gas-phase breakdown occurs, is reached at the breakdown voltage, the current abruptly increases 10^6–10^7 times, and the dark gas phase changes to the luminous gas phase. On this transformation, the electric field profile changes to the corresponding plasma sheath, which is recognized as the cathode fall region in the direct current (DC) glow discharge, and the electric field in the cathode fall is much higher than that in the dark gas phase [7]. It is important to emphasize that the cathode fall region, in which electrons are accelerated, does not exist in the dark (unbroken) gas phase, implying that the acceleration of electrons in the low electric field of the dark gas phase is insignificant.

According to the surface-state equilibration principle [8], the electrons in the surface state of the cathode metal could and should provide the primary electrons to cause the inception of glow discharge [7], which has not been considered in the classical interpretation. The electron emission from the cathode is a well-accepted phenomenon regardless of what causes it. The key issue is whether the ionization of gas by the primary electrons created in the gas phase initiates the electron avalanche, or the interfacial electron avalanche occurs first and causes the ionization of gas in the dielectrically broken-down gas phase. This paper describes the latter phenomena.

INTERFACIAL ELECTRON AVALANCHE AT THE ONSET OF LOW-PRESSURE ELECTRICAL DISCHARGE

The plot of the breakdown voltage, V_b, against ($p*d$), where p is pressure and d is the distance between the cathode and the anode, yields a curve with the minimum value of V_b, which is known as the Paschen curve as depicted in Fig. 1, which is obtained by plotting the data reported by Hassouba et al. using three different metals as the cathode [9]. Figure 1 shows that (1) the breakdown voltage of He, of which the ionization energy is greater than that of Ar, is lower than the breakdown voltage of Ar, (2) the minimum point for He occurs at higher value of $p*d$ (at higher pressure with a constant d), and (3) the value of breakdown voltage is dependent on the type of the cathode metal. These features are against the mechanism in which the ionization of gas is the first step for the breakdown of the gas phase, and indicate that the ionization energy of gas has no relevance to the gas-phase breakdown.

The parameter given by ($p*d$) is an insufficient parameter to describe the gas phase that exists in the inter-electrode volume, and the breakdown voltage is an insufficient parameter to describe the gas-phase breakdown; i.e., the analysis of breakdown process should use the parameters that describe the dark gas phase (before the transformation occurs) according to the fundamental principle of reaction kinetics. These fundamental principles are not followed in the traditional handling of the breakdown

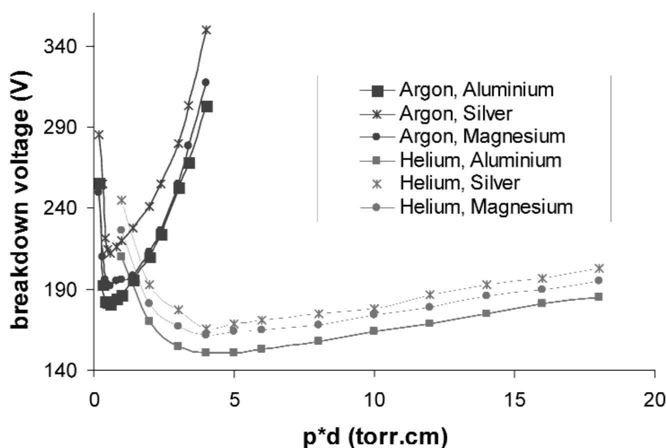

Fig. 1 Paschen curves as plots of the breakdown voltage against (*p*d*) for Ar and He with three different cathode metals: Al, Ag, and Mg [9].

process; i.e., analysis and calculation of parameters obtained in the broken-down gas phase are used to explain the breakdown process.

It is imperative to reckon that electron-impact reactions involved in the deposition plasma are mass interactions between an electron and a molecule by which the energy carried by the electron is transferred to the mass of the colliding gas. It is also important to point out that the initial step of gas-phase breakdown of a molecule (e.g., of trimethylsilane) has been intuitively assumed to be the same as that of an atomic gas (e.g., of argon) and that the presence of the dissociation glow invalidates such an assumption.

The electron-impact reactions are caused by the energy transferred to the mass of the gas atom or molecule by the impact of the energy-carrying electron, an interaction which is governed by energy delivered to the mass of gas and is given in J/kg. This process is totally different from the non-elastic collision of an electron and an atom that is used to explain the ionization and the excitation of an atom (e.g., of argon). In such a treatment, the effect of the difference of atoms (e.g., helium and argon) is explained by the size of gas atoms manifested by the cross-section of collision; however, the cross-section of collision between an electron and an atom cannot adequately explain the electron-impact ionization or excitation of an atom, because the size of the electron is too small to influence the collision cross-section beyond the cross-sectional size of the atom itself. Furthermore, the experimentally observed cross-section of ionization is highly dependent on the electron energy in a low-pressure domain [10], which is due to the fact that the wave (vs. particle) characteristics of electron beam become significant in low pressure. A brief explanation of Hatta's illustration in ref. [10] (in Japanese) is given in a book on plasma polymerization [11]. Since the cumulative gained-energy (from electrons) causes the dissociation of molecules, the concept of the electron-gas molecule collision based on the classical model of spherical balls colliding has little relevance in the deposition plasma.

The pressure of a gas system defines the total number of gas atoms or molecules. Therefore, in dealing with an electron-impact reaction, which is a mass action, it is mandatory to include the mass of gas (molecule or atom); i.e., instead of $p*V/R*T$, $p*V*M/R*T$, where M is the mass of gas, should be used.

There is an interesting contrast and an essential similarity in dealing with the controlling parameter of phenomenon and the experimentally manipulatable parameter in phenomena in dilute solution and electron-impact reactions in the gas phase. The freezing-point depression, the boiling-temperature elevation, and the osmotic pressure are colligative properties of dilute solution; i.e., the number of

solutes controls the phenomena, while experimentally manipulatable parameter is the mass in unit volume.

The electron-impact reactions in the gas phase are controlled by the mass of gas, while the experimentally manipulatable parameter is the number of gas derived from the pressure and volume. The essential similarity is that the experimentally manipulatable parameter is not the controlling parameter of the phenomena, and the manipulatable parameter must be converted to the controlling parameter of the respective phenomenon in order to comprehend the principle of phenomena.

Since two gases (Ar and He) are included in Fig. 1, these data could be used to demonstrate the importance of the mass by simply plotting the same data using $p*d*M$ as x-axis, which is shown in Fig. 2. The Paschen minimums for Ar and He occur at the identical $p*d*M$ scale, indicating the importance of the mass in the electron-impact reactions.

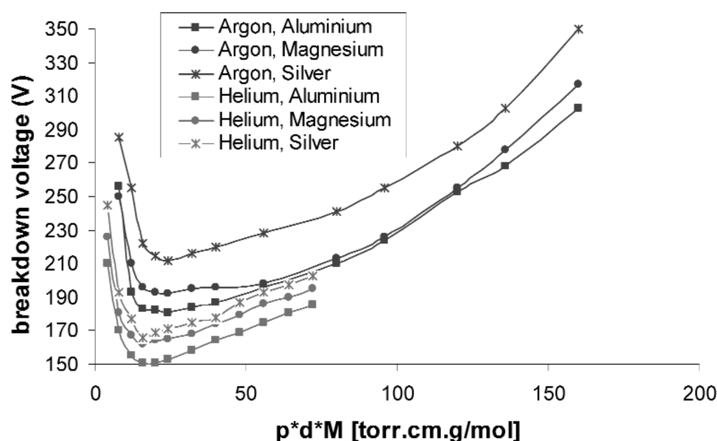

Fig. 2 Modified Paschen curves through modifying the x-axis as $p*d*M$, which show identical behaviors for Ar and He with respect to the location of the minimum breakdown voltage, for the data shown in Fig. 1.

If the electric field in the dark gas phase just before the gas-phase breakdown occurs, instead of the breakdown voltage, which is given by $V/(p*d*M)$, is used in the Y-axis, and the gas-phase parameter, which is given by $p*d*M$, is used for the X-axis, the modified Paschen curves (based on the parameters in the dark gas phase) appear as shown in Fig. 3, in which data points for Ar and He are on the same curve (except the effect of the cathode metal), indicating that the ionization of gas is not involved in the breakdown process.

The electron flux observed at the onset of glow discharge is found to be proportional to the calculated number of electrons in the surface state of metals, which supports the mechanism that primary electrons in the gas phase are provided mainly by the interfacial electron-transfer mechanism at the metal/gas interface.

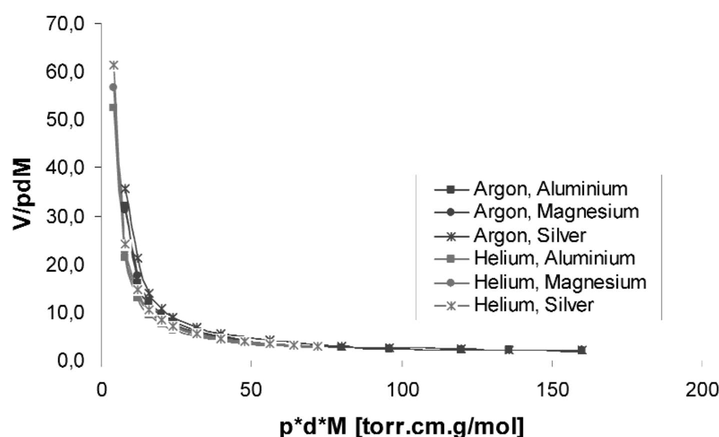

Fig. 3 Modified Paschen curves for Ar and He, with the *x*-axis $p*d*M$ and the *y*-axis $V/(p*d*M)$, using the data shown in Fig. 1.

We have conducted breakdown experiments for Ar and He with eight different metals with two surface areas each. Figure 4 depicts the correlation between the breakdown current of Ar DC discharge in the Paschen point and the calculated number of free electrons available at the surface state of each metal used in experiments. The breakdown current, under the occurrence of electron avalanche, is considered as the electron flux at the breakdown; i.e., no ion is involved at this stage. The linear correlation is a direct proof of the electron avalanche mechanism, which can explain the phenomena that DC discharge of different types of gases show different characteristics at different gas-phase excitation zones (see Fig. 7).

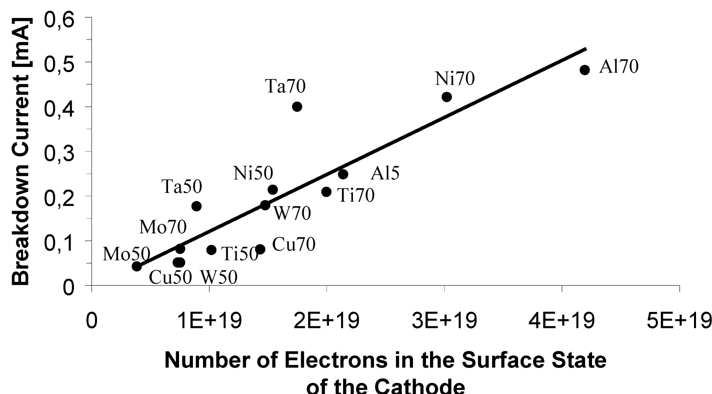

Fig. 4 Correlation between breakdown current and number of free electrons available in the surface state of cathode; the number indicates the diameter (mm) of cathode.

IMPLICATIONS OF THE ELECTRON AVALANCHE MECHANISM

In the gas phase in which ions are formed by the impact of energetic electrons, the electrical neutrality in the system cannot be assumed. An ionizing collision of an energetic electron with an atom yields one (low-energy) ion and two (low-energy) electrons. The electron-impact formation of neutral excited species does not consume electron. Considering elastic collisions (ineffective energy transfer), the system consists of a large number of electrons per ion. In such an electron-rich environment, the life-time

of ions formed in low-pressure discharge is bound to be very short because the out-numbering highly mobile electrons would neutralize ions.

In consideration of the electron flux from the cathode surface to the luminous gas phase, it is inconceivable that a large number of ions collide with the cathode surface. Therefore, it is warranted to re-examine other phenomena that have been explained by the bombardment of energetic ions on the cathode surface.

Magnetron plasma polymerization and sputtering

It had been considered that sputtering occurs as a plasma-enhanced thermal process (e.g., thermal evaporation) during the approximate period of 1935–1955. Since then, the concept of the momentum exchange principle has been prescribed widely [11,12]. Both mechanisms assume the bombardment of accelerated ions on the cathode surface. However, this mechanism is in contradiction to the classical mechanisms of the secondary electron emission for the inception of glow discharge.

In the reactor used for magnetron plasma polymerization and for magnetron sputtering, the impingement of accelerated ions onto the cathode surface is unlikely to occur in the magnetron discharge of Ar because of the high electron flux from the cathode surface close to the toroidal glow (toroidal cathode surface). The same audio frequency (AF) (15 kHz) magnetron discharge reactor can be used to perform either plasma polymerization or sputter coating by selecting a proper gas, the cathode metal, and the level of energy input suitable for the objective of the chosen process.

The effect of the magnetic field strength on Ar glow discharge revealed that the magnetic field decreases the discharge voltage and increases the current, while the sputter coating rate increases with increasing magnetic field strength as depicted in Fig. 5 [13]. This dependency is in accordance with the fact that the electron density in the toroidal glow of the magnetron glow discharge is very high and the electron temperature is very low [14], but contradicts the basic requirement that the higher voltage is necessary to increase the momentum of accelerated ions. These facts imply that the magnetron-sputtering of the cathode metal, at least within the framework of the experiments given, does not occur by the momentum exchange mechanism.

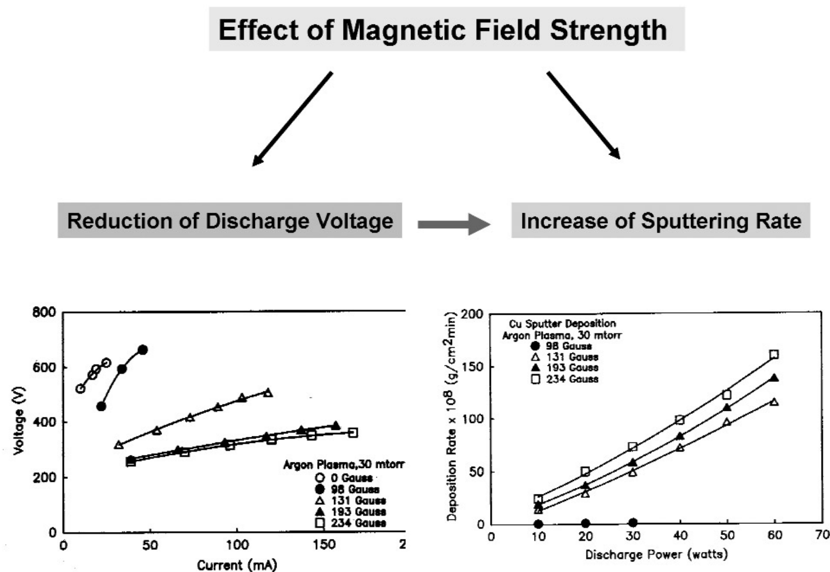

Fig. 5 Effect of magnetic field strength on the discharge-voltage and -current, and the rate of sputter coating of Cu.

When magnetron plasma polymerization of methane is performed, the polymer does not deposit onto a part of the electrode surface corresponding to the toroidal glow (in the gas phase), which is a unique advantage of the magnetron plasma polymerization and enables us to operate the stable plasma polymerization continuously for a long time (e.g., over a month). When the same magnetron is used for Ar discharge with Cu electrode, the ablation of Cu from the surface occurs at exactly the same location on the electrode surface where no polymer deposition occurred in the magnetron plasma polymerization, which implies that the same principle governs both phenomena. Namely, the high electron flux from the toroidal glow electrode surface prevents the deposition of plasma polymer and also causes the ablation of Cu atoms from the surface in Ar discharge.

The high electron flux from the surface state of the cathode metal dislodges atoms from the surface leading to the ablation of metal from the surface, which could be viewed as "interfacial electron avalanche induced ablation". Although this interpretation does not consider the bombardment of ions on the cathode surface or the consequential thermal evaporation, it is on the side of the earlier interpretation (evaporation) with respect to the mechanism of dislodging the atoms from the metal surface.

Principle of plasma polymerization

It is quite clear that the energy input into the luminous gas phase, or low-pressure plasma, does not occur uniformly into the whole gas phase. Instead, the creation of chemically reactive species necessary for plasma polymerization takes place in the relatively narrow band of the dissociation glow, of which location differs depending on the nature of glow discharge (i.e., DC, AF, AF magnetron, RF, etc). The shift of the location of dissociation glow within the same reactor depending on DC, AF (15 kHz), AF (15 kHz) magnetron, and RF (13.5 MHz) is schematically depicted in Fig. 6. So far as the plasma polymerization is concerned, DC and AF discharge is identical, and AF and AF magnetron are significantly different due to the shift of the dissociation glow from the surface to the gas phase. AF magnetron and RF discharge is somewhat similar because the dissociation glow is in the gas phase near the electrode surface. Because of oscillating motion of the electron in RF discharge, however, the influence of the magnetic field diminishes in RF magnetron discharge.

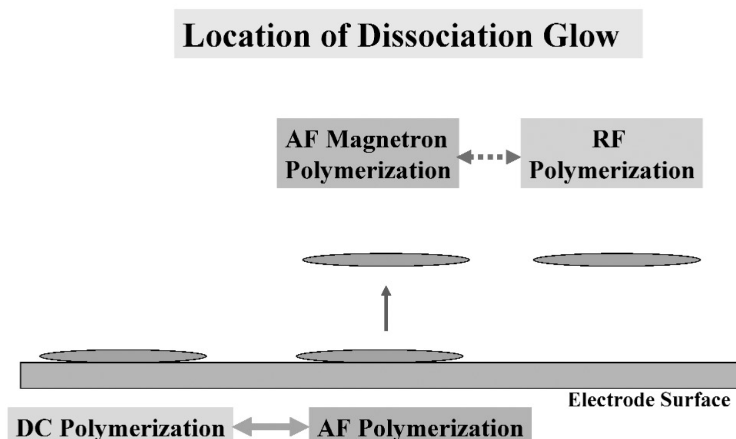

Fig. 6 Location of dissociation glow that controls the plasma polymerization.

Plasma sheath and sheath potential

Langmuir used the term "plasma" to describe the luminous gas phase created by glow discharge [17], and used the term "plasma sheath" for the boundary zone of plasma and the contacting surface. The

plasma sheath is the surface state of plasma in contact with a surface according to the concept of the surface-state equilibration principle. There are two different sheaths existing in low-pressure plasma. One is the energy-input sheath such as the cathode fall region of DC discharge of Ar, to which Langmuir referred in introducing the term "plasma", for the first time, for the non-sheath region of arc discharge of mercury vapor. The other is the energy-dissipating sheath between plasma and surfaces, which is the only sheath in the equilibrium plasma. The ionic concept of plasma polymerization is based on the second sheath, while the free radical concept of plasma polymerization emphasizes the first sheath that is the dissociation glow in the deposition plasmas.

The plasma sheath potential in weakly ionized plasma (luminous gas phase caused by electron-impact reactions) is the differential energy across the sheath, not the electric potential between plasma and the surface, which is solely determined by the energy level of plasma phase and of the surface. The profile of differential potential in both (energy-input and energy-dissipating) plasma sheathes might look alike; however, the energy flux is in the opposite direction. Dealing with RF plasma polymerization, the term "plasma sheath" has been used without specifying which type. Namely, "plasma sheath" is used more or less synonymously to the dissociation glow (i.e., the zone where chemically reactive species are formed).

The dissociation glows in RF plasma polymerization are in the gas phase near the electrode surface, which resembles the cathode fall region in DC discharge of Ar (energy-input plasma sheath for the ionization glow of Ar). Therefore, the dissociation glow of RF plasma polymerization could have been conceived as the equivalent of the cathode fall region in DC deposition plasma (without knowledge of the system dependency of plasma processes and of the dissociation glow). However, the differential (electric) potential of the energy-dissipating plasma sheath has been considered to be important in the deposition plasma according to the ionic concept of plasma polymerization.

The electrical potential gradient in the energy-dissipating plasma sheath would play a role in the deposition step of the reactive species; however, ions seem to have little influence in the overall growth mechanism because ions (mostly positive ions) repel each other, preventing the growth of reactive species, and the overall concentration of neutral species outnumber that of ions in the order of 10^6 in the deposition plasma [17].

Negative ions, on the other hand, seem to play a key role in the deposition plasma of some F-containing monomers according to the analysis of negative glow in the anode magnetron discharge. The magnetic shaping of the negative glow by the magnetron anode [7] is conspicuously absent with some F-containing monomers.

System dependency of low-pressure plasma processes

Figures 7 and 8 depict the system dependency of low-pressure plasma processes clearly evident in the respective glow. Those processes are obviously not identical and cannot be treated by the same mechanism. It should be borne in mind that the chemically reactive species are created in the dissociation glow, not in the whole luminous gas phase (glow). The low-pressure plasma processes are strongly dependent on the system in which the processes are carried out, because the electron dynamics is not the same in different systems. Therefore, the principle, mechanism, and trends found in a particular system should not be extended to other systems without examining the validity. For example, the mechanism of creating glow discharge of Ar in a DC discharge should not be extended to an RF discharge of methane. Similarly, the reaction scheme found with the plasma polymerization of fluorocarbons should not be extended to the principle of polymerizations of hydrocarbons, nor vice versa.

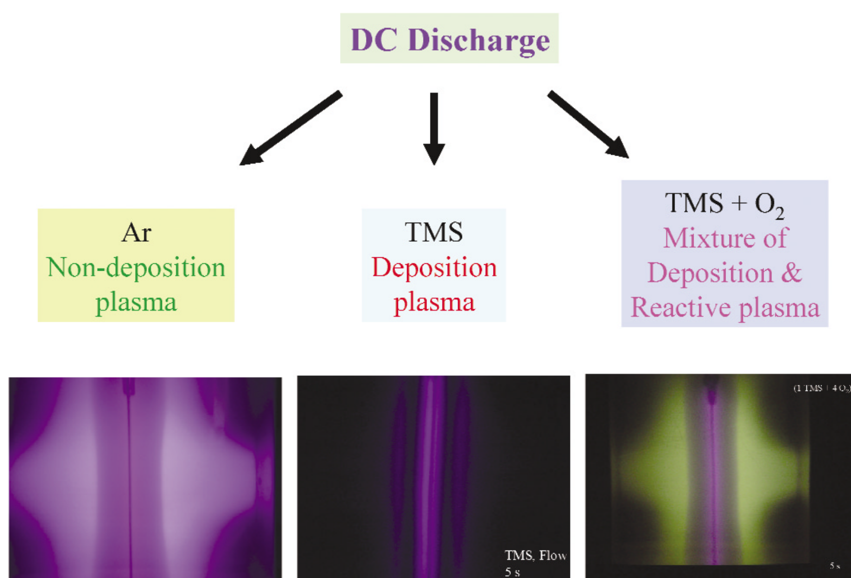

Fig. 7 Characteristics of glows of DC discharge of Ar, trimethylsilane (TMS), and a mixture of TMS and O_2.

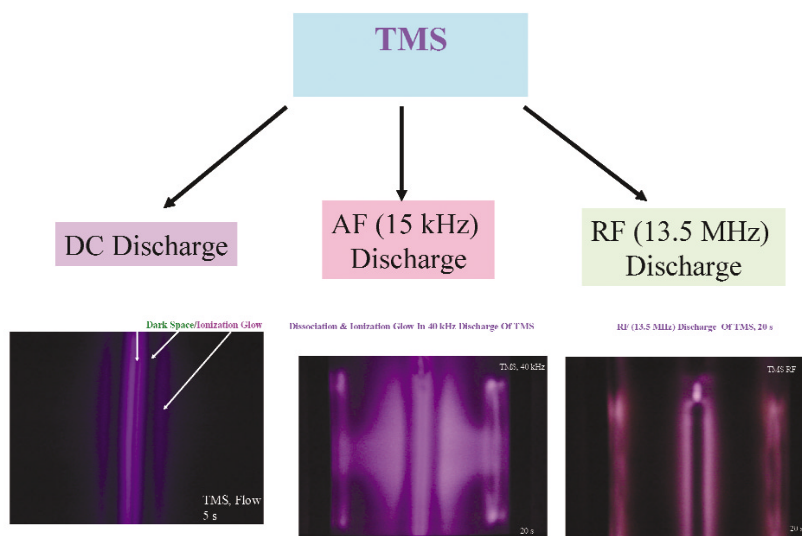

Fig. 8 Characteristic glows of TMS in DC, AF (15 kHz), and RF (13.5 MHz) discharges.

SUMMARY

The luminous gas phase created by low-pressure discharge by means of various power sources and coupling methods is an electron dynamics-dominated excited gas phase, which is far from the plasma in which the electron neutrality is maintained. The electron-impact ionization of gas yields electron-rich (against ions) gas phase, and the life-time of ions is very short. When the electric field in the dark gas phase reaches the threshold electric field of the dielectric breakdown of gas phase, the interfacial electron avalanche of the primary (free) electrons from the cathode surface to the gas phase occurs and creates a luminous gas phase. This process is not caused by the bombardment of ions as classical treatment

suggests; i.e., "secondary electron emission" is a misinterpretation of the primary electron avalanche. The primary electron avalanche causes glows characteristic of the nature of gas employed. Electron-impact reactions in the deposition plasma are caused by the cumulative mass interactions of energetic electrons with gas atoms or molecules, and the ionization energy of gas is irrelevant to the gas-phase breakdown. Hence, the inclusion of mass of gas in the gas-phase parameters is imperative in the elucidation of the gas-phase breakdown process. The knowledge of the system dependency of low-pressure plasma processes is important in elucidating mechanisms of plasma polymerization and also in utilizing processes in large-scale industrial operations.

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