Atmospheric Non-Thermal Plasma Sources

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Abstract

Atmospheric non-thermal plasmas (ANTPs) have received a great deal of attention in the last two decades because of their substantial breakthrough in diverse scientific areas and today technologies based on ANTP are witnessing an unprecedented growth in the scientific arena due to their ever-escalating industrial applications in several state-of-the-art industrial fields. ANTPs are generated by a diversity of electrical discharges such as corona discharges, dielectric barrier discharges (DBD), atmospheric pressure plasma jet (APPJ) and micro hollow cathode discharges (MHCD), all having their own characteristic properties and applications. This paper deals with some fundamental aspects of gas discharge plasmas (GDP) and provides an overview of the various sources of ANTPs with an emphasis on dielectric barrier discharge.

Keywords: Atmospheric plasma, Non-thermal, Dielectric barrier discharge.

1. INTRODUCTION

Since the past two decades, considerable efforts have been made by the scientific and technological community to generate, sustain and utilize ANTP because of their numerous scientific and industrial applications. Growth and importance of atmospheric cold plasma technology can be realized by the fact that the scientific and technological utilization of ANTP has multiplied by several factors and its applications have expanded into a large number of fields such as in environmental engineering, aeronautics and aerospace engineering, biomedical field, textile technology, analytical chemistry, and several other areas too. The enormous promise of atmospheric non-thermal technology stems from its remarkable potential for being environment friendly & energy-saving, its flexibility & capability for creation of new products and its clear ecological advantages. Unique features, diversified applications and a vast array of opportunities offered in a large number of diverse and unrelated fields has made it indispensable enough to harness their potential in the scientific and industrial areas. Keeping in view the huge potential of GDPs in several diversified fields, this article serves to

provide an overview of atmospheric non-thermal plasma. Most of the earlier studies on man-made plasmas were focused at low pressure, but the last two decades have witnessed a growing attention to generate GDP at elevated pressure, preferably close to atmospheric pressure. This is a challenging task due to instabilities of glow to arc transitions. At present, several approaches are being used to produce ANTP, out of which a few common approaches have been briefly discussed in this paper [1-11].

The paper is mainly divided into two parts. For a better understanding of the phenomena of GDP, one should have an acquaintance of the various parameters that one has to deal with in the gas discharges. Some of these fundamental aspects of GDP are discussed in the first half of the paper. The succeeding section mainly focuses on commonly used ANTP schemes such as corona, APPJ, MHCD, and DBD.

2. FUNDAMENTAL ASPECTS OF GDP

2.1 Plasma: Introduction

Plasma, a quasi-neutral gas, is considered to be the fourth state of matter, following the more familiar states of solid, liquid & gas and constitutes more than 99% matter of the universe. It is more or less an electrified gas with a chemically reactive media that consists of a large number of different species such as electrons, positive and negative ions, free radicals, gas atoms and molecules in the ground or any higher state of any form of excited species (fig. 1). It can exist over an extremely wide range of temperature and pressure. It can be produced at low-pressure or atmospheric pressure by coupling energy to a gaseous medium by several means such as mechanical, thermal, chemical, radiant, nuclear, or by applying a voltage, or by injecting electromagnetic waves and also by a combination of these to dissociate the gaseous component molecules into a collection of ions, electrons, charge-neutral gas molecules, and other species. It is thus an energetic chemical environment that combines particles and radiations of a diverse nature, an incredibly diverse source of chemistry that is normally not available in other states of matter. Parallel to the generation of plasma species, loss processes also take place in the plasma. In fact, all energy ends up as heat with a small fraction invested in surface chemistry.

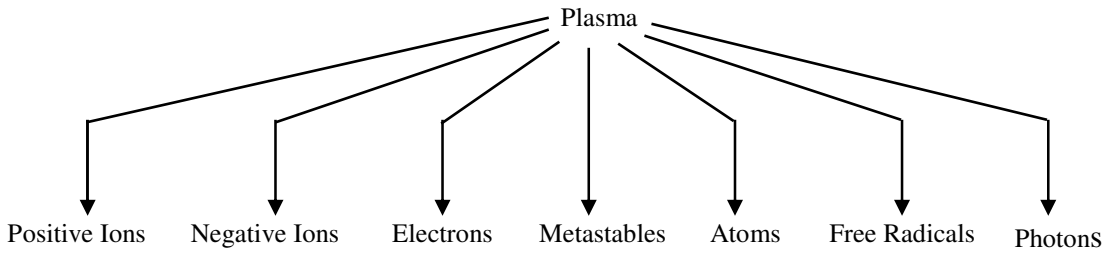

Figure 1: Constituents of plasma

2.2 Classification of plasma

Broadly speaking, plasmas can be distinguished into two main groups *i.e.,* the high temperature or fusion plasmas and the so called low temperatures or gas discharges. A typical classification and parameters of different kinds of plasmas is given in table 1. High temperature plasma implies that all species (electrons, ions and neutral species) are in a thermal equilibrium state. Low temperature plasma is further subdivided into thermal plasma, also called quasi-equilibrium plasma, which is in a local thermal equilibrium (LTE) state, and non thermal plasma (NTP), also called nonequilibrium plasma or cold plasma.

Plasma	State	Example
High temperature plasma (Equilibrium plasma)	$T_e \approx T_i \approx T_g, T_p = 10^6 - 10^8 K$ $n_e \geq 10^{20} m^{-3}$	Laser fusion plasma
Low temperature plasma		
Thermal plasma (Quasi-equilibrium plasma)	$T_e \approx T_i \approx T_g \leq 2 \times 10^4 K$ $n_e \geq 10^{20} m^{-3}$	Arc plasma, plasma torches, RF inductively coupled discharges
Non thermal plasma (Non-equilibrium plasma)	$T_e >> T_i \approx T_g = 300.....10^3 K$ $n_e \approx 10^{10} m^{-3}$	Glow, corona, APPJ, DBD, MHCD, OAUGDP, plasma needle etc

Table1: Classification of plasma

Thermal plasmas (TP) are characterized by an equilibrium or near equality between electrons, ions and neutrals. Commonly employed thermal plasma [12-20] generating devices are those produced by plasma torches, and microwave devices. These sources produce a high flux of heat and are mainly used in areas such as in plasma material processing and plasma treatment of waste materials. High temperature of TPs can process even the most recalcitrant wastes including municipal solids, toxic, medical, biohazard, industrial and nuclear waste into elemental form, ultimately reducing environmental pollution caused due to them. But for several technological applications, the high temperature characteristic of TPs is neither required nor desired, and in some cases it even becomes prohibitive. In such application areas, cold plasmas become more suited.

Cold plasmas refer to the plasmas where most of the coupled electrical energy is primarily channeled to the electron component of the plasma, thereby producing energetic electrons instead of heating the entire gas stream; while the plasma ions and neutral components remain at or near room temperature. Because the ions and the neutrals remain relatively cold, this characteristic provides the possibility of using cold plasmas for low temperature plasma chemistry and for the treatment of heat sensitive materials including polymers and biological tissues. The remarkable characteristic features of cold plasma that include a strong thermodynamic non-equilibrium nature, low gas temperature, presence of reactive chemical species and high selectivity offer a tremendous potential to utilize these cold plasma sources in a wide range of applications.

2.3 Plasma chemistry and origin of species

The chemistry [10, 21-22] which takes place in a plasma is usually quite complex and involves a large number of elementary reactions. The main types of reactions occurring in volume plasma are divided into homogenous and heterogenous reactions. Homogenous reactions occur between species in the gaseous phase as a result of inelastic collisions between electrons and heavy species or collisions between heavy species; whereas, heterogenous reactions occur between the plasma species and the solid surface immersed or in contact with the plasma. These typical reactions have been listed in table 2 (a) and (b). The heterogenous reactions are particularly important in the processing of semiconductor materials.

Name	Reactions	Description
Excitation of atoms or molecules	$e + A_2 \rightarrow A_2^* + e$ $e + A \rightarrow A^* + e$	Leads to electronically excited state of atoms and molecules by energetic electron impact.

De-excitation	$e + A_2^* \rightarrow A_2 + e + hv$	Electronically excited state emits electromagnetic radiations on returning to the ground state.
Ionization	$e + A_2 \rightarrow A_2^+ + e$	Energetic electrons ionize neutral species through electron detachment and positively charged particles are formed.
Dissociation	$e + A_2 \rightarrow 2A + e$	Inelastic electron impact with a molecule causes its dissociation without ions.
Dissociative attachment	$e + A_2 \rightarrow A^+ + A + e$	Negative ions are formed when free electrons attach themselves to neutral species.
Dissociative ionization	$e + A_2 \rightarrow A + e$	Negative ions can also be produced by dissociative ionization reactions.
Volume recombination	$e + A + B \rightarrow A + B$	Loss of charged particles from the plasma by recombination of opposite charges.
Penning dissociation	$M^* + A_2 \rightarrow 2A + M$	Collision of energetic metastable species with neutral leads to ionization or dissociation.
Penning ionization	$M^* + A \rightarrow A^+ + M + e$	
Charge exchange	$A^+ + B \rightarrow B^+ + A$	Transfer of charge from incident ion to the target neutral between two identical or dissimilar partners.
Recombination of ions	$A^- + B^+ \rightarrow AB$	Two colliding ions recombine to form a molecule.
Electron–Ion recombination	$e + A_2^+ + M \rightarrow A_2 + M$	Charge particles are lost from the plasma by recombination of opposite charges.
Ion-ion recombination	$A^+ + B^- + M \rightarrow AB + M$	Ion-ion recombination can take place through three body collisions.

Table 2 (a): Gas phase reactions involving electrons and heavy species

Name	Reactions	Description
Etching	$AB + C_{solid} \rightarrow A + BC_{vapour}$	Material erosion.
Adsorption	$M_g + S \rightarrow M_s$ $R_g + S \rightarrow R_s$	Molecules or radicals from a plasma come in contact with a surface exposed to the plasma and are adsorbed on surfaces.
Deposition	$AB \rightarrow A + B_{solid}$	Thin film formation.
Recombination	$S - A + A \rightarrow S + A_2$ $S - R + R_1 \rightarrow S + M$	Atoms or radicals from the plasma can react with the species already adsorbed on the surface to combine and form a compound.
Metastable de-excitation	$S + A^* \rightarrow A$	Excited species on collision with a solid surface return to the ground state.

Sputtering	$S - B + A^+ \rightarrow S^+ + B + A$	Positive ions accelerated from the plasma towards the surface with sufficient energy can remove an atom from the surface.
Polymerization	$R_g + R_s \rightarrow P_s$ $M_g + R_s \rightarrow P_s^{\cdot}$	Radicals in the plasma can react with radicals adsorbed on the surface and form polymers.

Table 2 (b): Surface reactions

2. 4 Electrical breakdown of gases

2.4.1 Conditions for self sustained discharge

To sustain plasma, the applied voltage must exceed the breakdown voltage for the gases. When this voltage is reached, the gases lose their dielectric properties and turn into a conductor. The criteria for self sustaining is given as

$$1 - \gamma\left(e^{\alpha d} - 1\right) = 0$$

$$e^{\alpha d} = \left(1 + \frac{1}{\gamma}\right)$$

2.4.2 Paschen breakdown criteria

The breakdown voltage in gas discharge plasma is given as

$$V_b = \frac{Bpd}{\{\ln(Apd) - \ln[\ln(1 + \frac{1}{\gamma})]\}} \qquad (1)$$

$V_b = f(pd)$, which is the Paschen law.

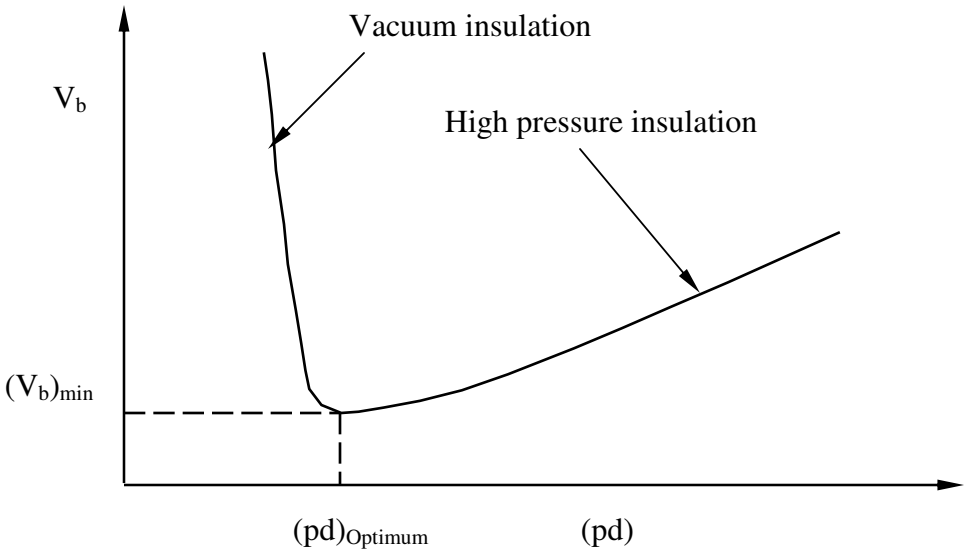

Figure 2: Paschen curve for breakdown voltage versus pd

From (1) it is obvious that breakdown voltage depends only on the product pd for a given gas and the cathode material, regardless of the individual values of p and d. The Paschen curves (fig. 2)

for different gases have roughly the same shape but are shifted from one another. From the curve, it is clear that there is a minimum breakdown voltage at a certain pd product and the breakdown potential is large for both small and large values of pd. At low pd values, the breakdown voltage is high because of too few collisions and at high pd values; the breakdown voltage is high because of too many collisions. The physical significance of this minimum voltage is that no matter how small the gap or pressure, it is impossible to strike a discharge at a voltage less than the minimum breakdown voltage [22-23].

3. ATMOSPHERIC NON-THERMAL PLASMA SCHEMES

Low pressure glow discharge plasmas are of great interest in fundamental research as well as in the microelectronic industry and material technology. But, these plasmas must be contained in costly air tight enclosures (massive vacuum reactors) making them highly expensive and time consuming. Also, the density of activated particles is relatively low. Therefore, one of the recent trends focuses on developing new plasma sources, which operate at atmospheric pressure, but retain the properties of low pressure media. The economic and operational advantages of operating at 1 atm have led to the development of a variety of atmospheric plasma sources for several scientific and industrial applications.

Thus, in the last two decades, ANTPs have attracted more attention due to their significant industrial advantages over low-pressure discharge. Non-thermal atmospheric plasma may be obtained by a diversity of electrical discharges such as corona discharge, micro hollow cathode discharge, atmospheric pressure plasma jet, gliding arc discharge, one atmospheric uniform glow discharge, dielectric barrier discharge, and plasma needle, all having important technological applications. The characteristic of all these atmospheric plasma sources in terms of plasma properties is shown in table 3. A brief description of commonly used forms of ANTP is illustrated in the succeeding sections.

Parameters	Corona Discharge	DBD	APPJ	Atmospheric glow MHCD
Method and Type	Sharply pointed electrode	Dielectric barrier cover on electrodes	RF capacitvely coupled	DC glow with micro hollow cathode electrode
Excitation	Pulsed DC	AC or RF	RF 13.5 MHz	DC
Pressure (bar)	1bar	1bar	760 torr	1bar
Electron energies (eV)	5 variable	1-10	1-2	……..
Electron Density, cm^{-3}	10^{9}-10^{13} variable	≈10^{12} -10^{15}	10^{11}-10^{12}	
Breakdown Voltage (kV)	10-50	5-25	0.05-0.2	…….
Scalability & Flexibility	No	Yes	Yes	Yes
T_{max} Temp T (K)	Room	Average gas Temp (300)	400	2000
Gas	……..	N_2+ O_2+ NO+ Rare gas/Rare gas halides	Helium, Argon	Rare gas Rare gas/Rare gas halides

Table 3: Plasma properties of atmospheric discharge schemes

3.1 Corona discharge

The first scheme that was used to generate ANTP was corona discharge [1, 2, 24-26]. It exists in several forms, depending on the polarity of the field and the electrode geometrical configuration. This type of discharge is the characteristic of an asymmetric electrode pair and results from the electric field that surrounds inhomogenous electrode arrangements powered with a continuous or pulsed dc voltage. In a highly non-uniform electric field, as for example, point plane gap or wire cylindrical gap, the high electric field near the point electrode or wire electrode far exceeds the breakdown strength of the gas and a weakly ionized plasma is created. Coronas are thus inherently non-uniform discharges that develop in the high field region near the sharp electrode spreading out towards the planar electrode. This phenomenon of local breakdown is called corona discharge. Fig. 3 shows a schematic of point to plane corona. It is a positive corona when the electrode with the strongest curvature is connected to the positive output of power supply and a negative corona when this electrode is connected to the negative terminal of power supply. The development of a corona discharge progresses sequentially through the following steps: (1) an asymmetric electrode configuration is made; (2) a high voltage is applied, and some free electric charge is made available; (3) an avalanche builds up and leaves behind a space charge area; (4) photons from the avalanche create new charge carriers outside the space charge area; (5) a new avalanche develops closer to the cathode. The most important large-scale application of corona discharge is in electrostatic precipitators (ESP), which are used for dust collection in many industrial off gases. In addition to ESP, corona discharges are also used in water purification, electrophotography, copying machine, printers and liquid spray gun and in powder coating. However, the restricted area and the inherent non-uniformity have limited their application in material processing.

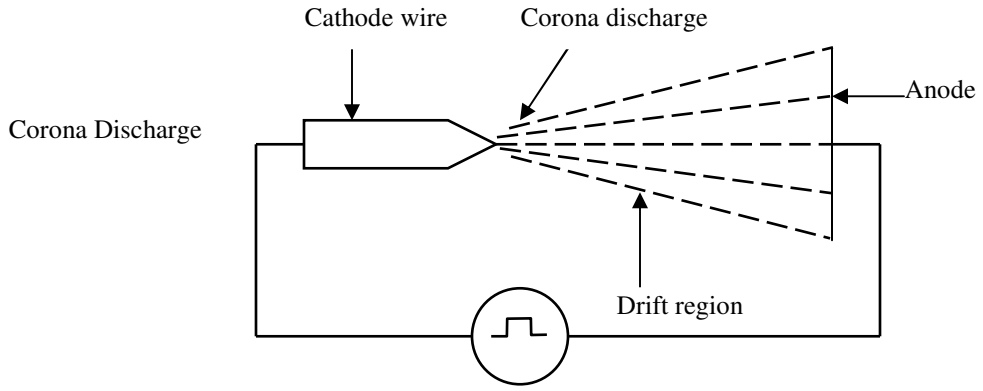

Figure 3: Schematic of corona discharge

3.2 Atmospheric-pressure plasma jet

Another kind of discharge capable of generating non-thermal plasmas at atmospheric pressure is atmospheric-pressure plasma jet. A schematic of the APPJ is shown in fig 4. The APPJ [27-32] developed by Jeong et al. (University of California, Los Angeles) in collaboration with Park et al. (Los Alamos National Laboratory) consists of two concentric electrodes through which a mixture of helium, oxygen or other gases flows. In this arrangement, the inner electrode is coupled to 13.56 MHz radio frequency power at a voltage between 100-250 V and the outer electrode is grounded. By applying RF power, the discharge is ignited and operates on a feed stock gas, which flows between an outer grounded, cylindrical electrode and a central electrode and produces a high velocity effluent stream of highly reactive chemical species. Central electrodes driven by radio frequency power accelerate free electrons. These energetic electrons undergo inelastic collisions with the feed gas, producing excited state molecules, atoms, free radicals and additional ion-electron pairs. Once the gas exits the discharge volume, ions and electrons are rapidly lost by recombination, but the fast flowing effluent still contains neutral metastable species and radicals. The key operational features of APPJ are as follows: (1) it produces a stable, homogenous and uniform

discharge at atmospheric pressure; (2) operates at radio frequency (RF) power of 250 W and frequency of 13.56 MHz ; (3) the ionized gas from the plasma jet exits through the nozzle where it is directed onto the substrate and hence utilized in downstream processing; (4) it operates without a dielectric cover over the electrode, yet is free from filaments, streamers and arcing; (4) The gas temperature of the discharge is as low as 50℃, allowing it to treat delicate surfaces without damage, or as high as 300℃, allowing it to treat robust surfaces much more aggressively. (5) it exhibits a great similarity to low-pressure DC glow discharge. This technology shows promises for being used in material application that are now limited to vacuum. These features give APPJ the potential to be utilized in a large number of applications. It has major utilization in material processing, for example, applications ranging from etching polyamide, tungsten, tantalum and silicon dioxide as well as to deposit silicon dioxide film by plasma assisted chemical vapor deposition. The fast flowing effluent of reactive species in APPJ technology is also utilized in applications such as decontamination of materials having chemical and biological warfare agents and in the removal of radionuclide from surfaces and equipments. In addition, it is also used to clean large industrial parts more effectively than solvents; sterilization of surgical and dental equipments and hospital surfaces and removal of paint from brick, making it effective for graffiti removal; and in the textile industry.

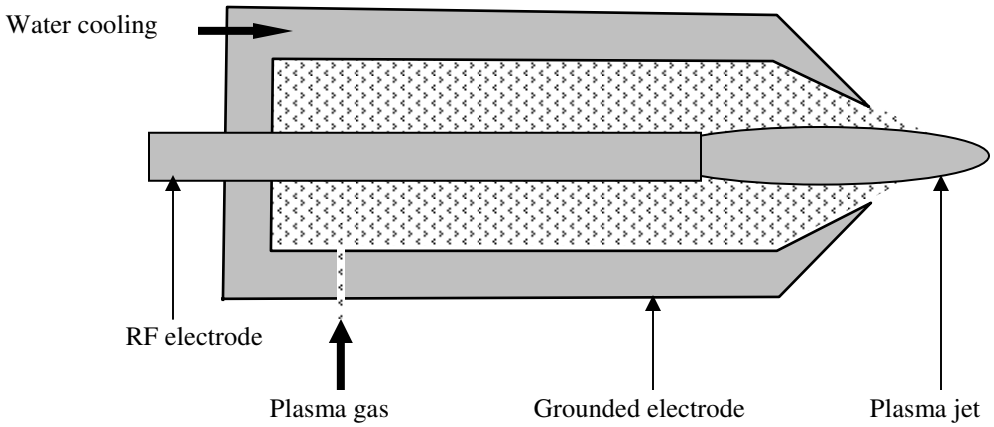

Figure 4: Schematic of atmospheric pressure plasma jet

3.3 Microhollow cathode discharge

A third approach to generate ANTP relies on the use of micro-hollow cathode electrode concept. The general idea is that the modification of cathode shapes in linear discharge lead to an increase in the current density by several orders of magnitude as compared to linear discharge. This kind of discharge with modified cathode is known as hollow cathode discharge (HCD). HCD [33] consists of a cathode, which contains some kind of a hole or a cavity or it may be a hollow cylinder, spherical segment or simply a pair of plane parallel plates, and an arbitrary shaped anode. The hollow cathode effect was originally used as a high current density electron source at low gas pressure for the development of high power pseudospark switches. The chief causes of electron generation in hollow cathodes include: (1) secondary electron emission from cathode due to ions and ultraviolet photons; (2) secondary electron emission due to bombardment of metastable atoms on the cathode, however, their flux flowing to the cathode is much smaller than that of ions; (3) pendulum or pendel effect for oscillatory motion of electrons between the opposite cathode surfaces under the influence of positive plasmas. In a specific range of values for the product *pD*, where *p* is the pressure and D the diameter of cathode bore, the current is enhanced by the pendulum motion of electrons. From a fundamental perspective, high-pressure operation of HCD can be accomplished by reducing the diameter of the bore to the values of the order of a few tens of micrometers; this hollow cathode effect can be obtained at atmospheric pressure. Thus, for atmospheric pressure discharges in hollow cathode, the typical hole diameter should be in micrometer range and

hence the term microhollow cathode discharge [34-38] arises because of the required small size of the cathode opening for high-pressure operation.

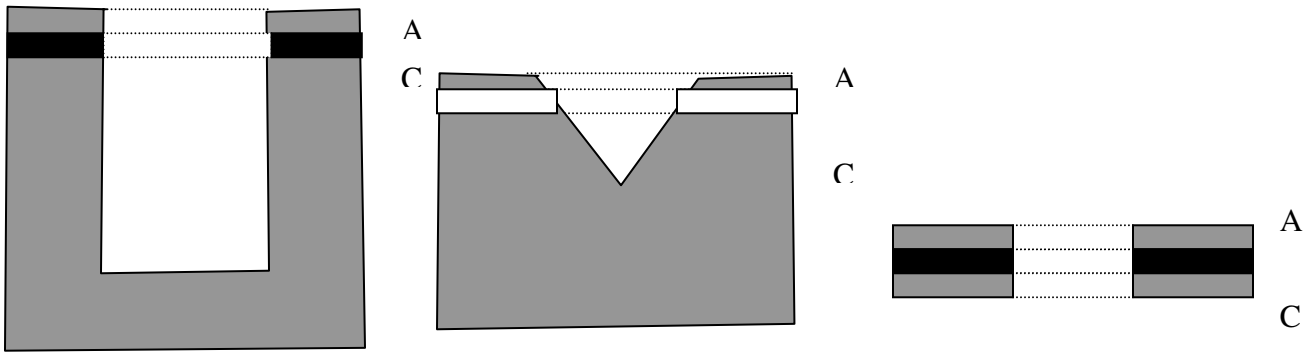

Figure 5: Typical electrode geometries of micro hollow cathode discharge [38]

The MHCD plasma may be operated in either direct current or pulse mode and two scaling laws largely determine its properties. The product (pd) of the pressure,p, and anode-cathode separation d obeys the well-known Paschen law, which determines the required breakdown voltage for a given value of p and d as well as the identity of the operating gas. A second scaling law, unique to the HCD involves the product (pD) in which D is the dimension of an aperture to the cathode. The similarity law for HCD is the basic effort to extend the pressure range for the hollow cathode discharge operation. The typical electrode geometries of MHCD are shown in fig.5. In fact, MHCDs are direct current high pressure, gas discharges between two plane parallel electrodes separated by thin layers of a dielectric material with a central borehole in each electrode. The thickness of the electrode material and the dielectric layers is in the range of 100μm, while the hole diameter varies between 100-200μm. MHCD plasmas have been utilized for several applications including remediation of gaseous pollutants, medical sterilization and biological decontamination, cleaning of metallic surfaces, diamond deposition etc. In addition to these applications, energetic electrons created by pendel effect efficiently generate excimers in MHCD. Such excimer sources can be operated over a wide range of wavelength in the ultraviolet and vacuum ultraviolet region.

3.4 Dielectric barrier discharge

Dielectric barrier discharge, also referred to as barrier discharge or silent discharge is a specific type of AC discharge, which provides a strong thermodynamic, non-equilibrium plasma at atmospheric pressure, and at moderate gas temperature. It is produced in an arrangement consisting of two electrodes, atleast one of which is covered with a dielectric layer placed in their current path between the metal electrodes. The presence of one or more insulating layer on/or between the two powered electrodes is one of the easiest ways to form non-equilibrium atmospheric pressure discharge. Due to the presence of capacitive coupling, time varying voltages are needed to drive the DBD. One of the major difference between the classical and a DBD discharge is that in a classical discharge, the electrodes are directly in contact with the discharge gas and plasmas, and therefore during the discharge process, electrode etching and corrosion occurs. On the contrary, in DBDs the electrode and discharge are separated by a dielectric barrier, which eliminates electrode etching and corrosion. Another fundamental difference is that the DBDs cannot be operated with DC voltage because the capacitive coupling of dielectric requires an alternating voltage to drive a displacement current. An AC voltage with amplitude of 1-100 kV and a frequency from line frequency to several megahertz is applied to DBD configurations. DBD cold plasma can be produced in various working mediums through ionization by high frequency and high voltage electric discharge. The DBDs unique combination of non-equilibrium and quasi-continuous behavior has motivated a wide range of applications and fundamental studies.

3.4.1 DBD Structure

The discharge burning [39-43] between two electrodes, at least one electrode insulated with a dielectric layer can be operated in a wide range of geometrical configurations such as the classical volume discharge, surface discharge, and coplanar discharge.

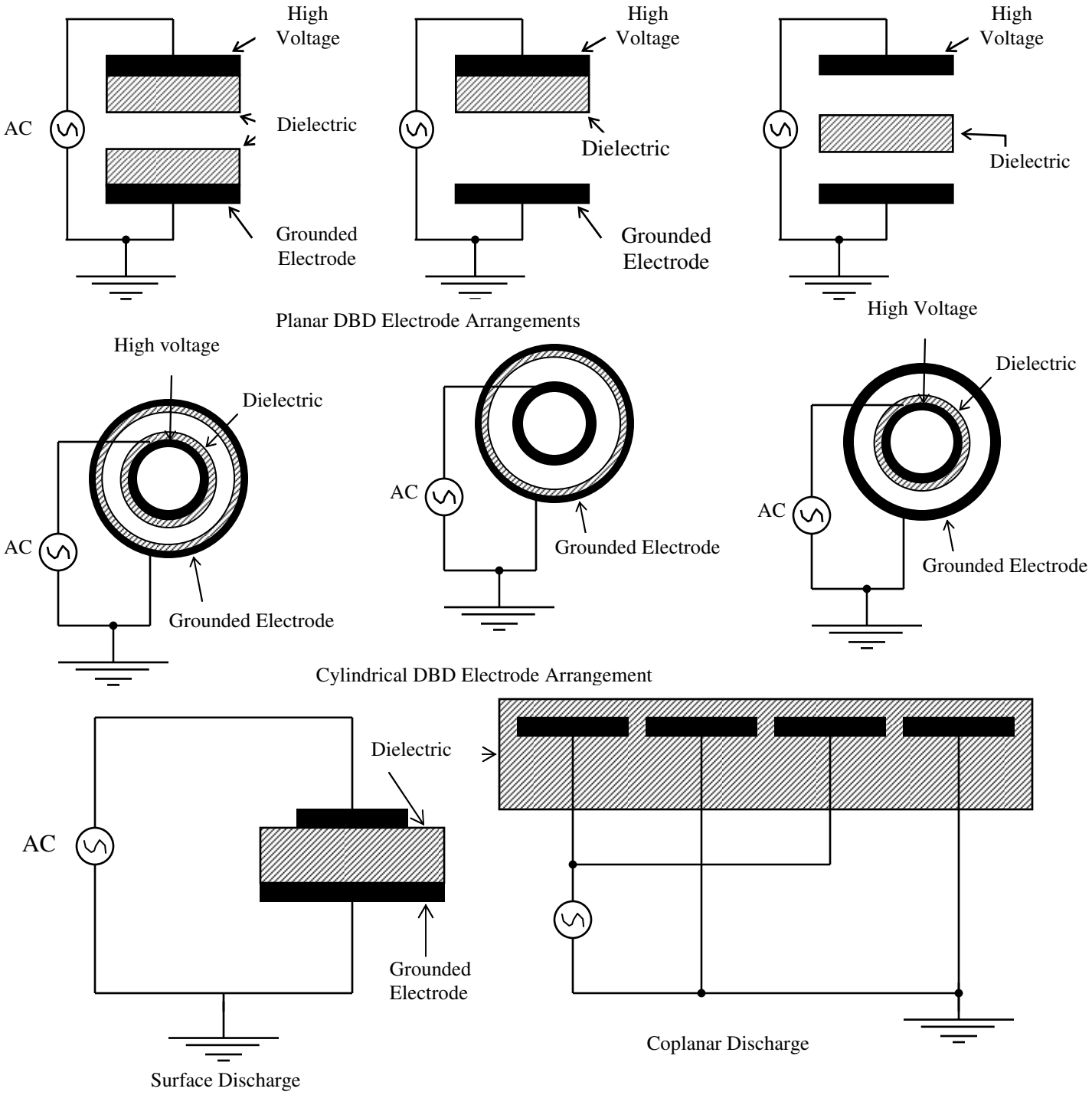

Figure 6: Typical electrode arrangements of DBD configurations

Volume discharges can also have either planar or coaxial arrangements. In planar electrode arrangements, the two electrodes are parallel to each other, and one or two dielectric barriers are always located either (i) on the powered or the ground electrode, or (ii) on both the electrodes, or (iii) in between the two metal electrodes. The electrodes in DBD can also be arranged in a coaxial manner having one electrode inside the other with at least one or two dielectric barriers located either (i) on the outer side of the inner electrode/on the inner side of the outer electrode, or (ii) on both the electrodes facing each other, or (iii) in between the two cylindrical electrodes. Besides the volume discharges, other designs also exist that use either surface or coplanar discharge geometry. Surface discharge [44] device have a thin and long electrode on a dielectric surface and an extended counter-electrode on the reverse side of the dielectric. In this configuration, the discharge gap is not clearly defined and so the discharge propagates along the dielectric surface. There also exist combinations of both volume and surface discharge configuration such as the coplanar arrangement [45-46] used in plasma display panel. The coplanar discharge device is characterized by pairs of long parallel electrodes with opposite polarity, which are embedded within a dielectric bulk nearby a surface. In addition to these configurations, other variants of DBD [47] are also used in various applications. The typical arrangements of DBD are shown in fig. 6.
DBD can exhibit two major discharge modes [48-49], either filamentary mode, which is the common form of discharge composed of many microdischarges that are randomly distributed over the electrode surface; or homogenous glow discharge mode, also known as atmospheric pressure glow discharge mode due to similarity with dc glow discharges.

3.4.2 Applications of DBD

DBD technologies have an incredible potential [50-55] and are widely used in a large number of technical applications. The advantage of DBD over other discharges lies in having the option to work with non-thermal plasma at atmospheric pressure and a comparatively straightforward scale-up to large dimensions. Initially, this technology was utilized for ozone production for the treatment of drinking water. Since then the number of industrial applications of this type of discharge have shown a tremendous growth. Besides ozone synthesis, today the phenomenon of DBD in gases is widely used in the generation of excimer radiation in the UV/VUV spectral regions, surface treatment, in the field of environment protection, for pumping CO_2 lasers, pollution control, various thin film deposition processes, in the textile industry, and more recently in plasma display panel and in several other technological processes in science and industry.

Out of all these applications of DBD, the excimer formation, one of the significant application area of DBD technology gained major impetus in the last decade. Excimer UVR optical source [56-64] is a particular configuration of DBD, specifically; a volume discharge. The acronym excimer refers to complexes with weakly bound excited state of molecules that under normal conditions do not possess a stable ground state. These excimers when they come to their ground state convert their binding energy into VUV/UV radiation. In the forthcoming section, the application of barrier discharge in this area has been elaborated.

For efficient excimer formation in non-thermal plasma (DBD & MHCD), three conditions need to be satisfied: (1) the bulk gas has to be provided with a large concentration of energetic electrons with energies above the threshold for the metastable formation or ionization; (2) since the formation of excimers is a three-body process, the gas pressure needs to be high, close to atmospheric in order to have sufficiently high rate of three body collisions. The high pressure is needed to ensure that the excimer formation reaction is faster than any quenching processes of the excited precursors; (3) the gas temperature has to be cold since excimers are thermally unstable. These conditions can only be effectively achieved in electron driven high-pressure non-thermal plasma processes occurring in DBD plasma.

The mechanism of excimer formation takes place with ionization and excitation of rare gas species by high-energy electrons. The dominant plasma chemical reactions for excimer formation can be described as follows:

A. Electron impact ionization and excitation

The high-energy electrons in DBD ionize and excite the rare gas species. In case of rare gas halides, the high energy electrons ionize and excite the rare gas atom, and at the same time, the halogen molecules are split by a dissociative attachment reaction

$$e + Rg \rightarrow e + Rg^*$$

$$e + Rg \rightarrow 2e + Rg^+$$

$$e + Rg^* \rightarrow e + Rg^{**}$$

$$e + X_2 \rightarrow X + X^-$$

B. Formation of excimers and exciplexs

The excimer molecule is formed by three body reactions of an electronically excited rare gas atom Rg* with other rare gas atoms or with a buffer gas in the ground state.

$$Rg^* + Rg + M \rightarrow Rg_2^* + Rg + M$$

$$e + Rg^{**} \rightarrow e + Rg_2^*$$

In case of rare gas/halogen mixtures, most RgX^* exciplexes are formed either by a three body ionic recombination of the positive rare gas ions and the negative halogen ions or by the Harpooning reaction in which the excited rare-gas species transfers its loosely bound electron to the halogen molecule or halogen containing compound to form an electronically excited state of RgX^*.

$$Rg^+ + X^- + M \rightarrow RgX^* + M$$

$$Rg^* + X_2 \rightarrow RgX^* + X$$

C. Emission of UV/VUV photon

These excimer or exciplex molecules are not very stable and once formed decompose within a few nanoseconds giving up their excitation energy in the form of UV or VUV photons.

$$Rg_2^* \rightarrow 2Rg + hv$$

$$RgX^* \rightarrow Rg + X + hv$$

Depending on the optical working media, a large number of different excimers can be generated in ANTP such as in DBD and MHCD.

4. CONCLUSION

In the present paper, a review of commonly used atmospheric non-thermal plasma sources has been presented. The unique features of non-thermal plasma have made possible substantial breakthroughs in many growth areas of modern technology and newer applications are continuously emerging, more recently in the vastly growing areas of nanotechnology, which indicate that the non thermal plasma has become an important player in several up-coming technologies. On the other hand, the prospect of using plasmas in numerous industrial applications without the need of any vacuum equipment has been driving the search for methods to generate atmospheric pressure non-thermal plasmas. While there is still more to go in the development and utilization of these plasma sources, no doubt that low temperature atmospheric pressure gas discharge plasma is a promising technology, not only for the future, but also for today's processes and applications. Looking ahead, still many opportunities remain to be harnessed for further research and development in order to meet the demand of various diverse plasma technological applications.

Note: T_e = electron temperature, T_i = ion temperature, T_n = neutral temperature, T_p = plasma temperature, n_e= electron density, Rg represents the ground state of rare gas species (eg., Ar, Kr, Xe, etc), X is a halogen species (eg., F, Cl, Br), Rg^* is a metastable state of neutral gas atom,

Rg^*_2 is the excimer, M is a collisional third partner, which in many cases can be an atom or molecule of the active species or even of the buffer gas. The symbols, A, B stand for atoms, A_2, B_2 for molecules, and e stands for an electron, M is a temporary collision partner, and species marked by + or – are ions, R, for a simple radical, and P, for a polymer formed in the plasma. The excited species are marked by asterisk (*), S-A indicates an atom adsorbed on the surface. The subscripts g and s indicate, respectively a species in the gas or solid phase. The term *hv* indicates release of radiation energy.

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