

# 1

## Plasma – The Fourth State of Matter

### 1.1 Fundamentals of Plasmas

The term “plasma” dates back to the year 1712 when it defined a form or shape (originally *plasm* in 1620), also originating from the Greek word “πλάσμα” denoting something molded or created. Later, the renowned Czech physiologist Jan Evangelista Purkinje (1787–1869) introduced the term plasma to describe the clear fluid which remains after all the corpuscular material in blood is removed.

A physical plasma was first identified in a Crookes tube, described by Sir William Crookes in 1879 as “radiant matter.” The physical nature of the Crookes tube matter was ultimately identified by British physicist Sir J.J. Thomson in 1897 and termed plasma by American scientist Irving Langmuir in 1928 to describe an ionized gas which he found could be manipulated by a magnetic field. Langmuir, a researcher who focused on understanding electric discharges, was the first person to apply the term to describe this type of ionization process. G.L. Rogoff provided the following explanation of Langmuir’s original application of the term [1]:

## 2 ATMOSPHERIC PRESSURE PLASMA FOR SURFACE MODIFICATION

"During the 1920s Irving Langmuir was studying various types of mercury-vapor discharges, and he noticed similarities in their structure – near the boundaries as well as in the main body of the discharge. While the region immediately adjacent to a wall or electrode was already called a "sheath," there was no name for the quasi-neutral stuff filling most of the discharge space. He decided to call it plasma.

"While his relating the term to blood plasma has been acknowledged by colleagues who worked with him at the General Electric Research Laboratory [2, 3], the basis for that connection is unclear. One version of the story has it that the similarity was in carrying particles, while another account speculated that it was in the Greek origin of the term, meaning "to mold," since the glowing discharge usually molded itself to the shape of its container [4]. In any case, it appears that the first published use of the term was in Langmuir's "Oscillations in Ionized Gases," published in 1928 in the *Proceedings of the National Academy of Sciences* [5]." Thereafter the term plasma was used to describe partially ionized gases. In addition to this contribution, Langmuir developed the theory of "plasma sheaths," expressed as the boundary layers which form between ionized plasmas and solid surfaces. Langmuir also discovered that certain areas of a plasma discharge tube exhibited variations in electron density, known today as "Langmuir waves." It is truly Langmuir's research which has formed the basis of *plasma processing* techniques used today for practical applications of plasmas, particularly the fabrication of integrated circuits.

And thus in this revolutionary period from the 1920s and into the 1940s, researchers were enabled to rapidly accelerate study of what we recognize today as plasma physics. This research was focused primarily on developing an understanding of the effect of ionospheric plasma on long distance shortwave radio propagation, and gaseous electron tubes used for rectification, switching and voltage regulation in the pre-semiconductor era of electronics. In the 1940s Hannes Alfvén developed a theory of hydromagnetic waves (now called Alfvén waves) and proposed that these waves would be important in astrophysical plasmas. In the early 1950s large-scale plasma physics-based magnetic fusion energy research started simultaneously in the USA, Britain and the then Soviet Union [6]. In the 1960s, space propulsion was advanced using plasma/ion-based thrusting technology. More relative to the subject matter of this writing, the 1980s saw the application of plasmas within the

newly evolving computer industry. Specifically, low pressure plasmas were developed and employed to fabricate ever-miniaturizing integrated circuitry.

Plasma is often referred to as the “fourth state of matter.” Although plasmas are omnipresent in virtually every home and business, they are not well understood. Approximately 99% of the visible universe is composed of plasma. Approximately 90% of the universe’s mass is thought to be present in “dark matter,” the composition and state of which are not known. Stars and interstellar space are examples of plasmas. From a local astrophysical perspective, the sun within our solar system, the interstellar space, the ionospheres of earth and the planets, as well as the ionospheres of comets all consist of plasmas. Because plasmas are composed of electrically charged particles, they are significantly influenced by electric and magnetic fields, although neutral gases are not. One example of this type of influence is energetic charged particles trapped along geomagnetic field lines which form the Van Allen radiation belts. Terrestrial plasmas span from natural lightning to uses with fluorescent lighting, arc welding, and the emissive displays of computers. Fundamentally, plasma is a state of matter as represented by a solid, liquid or gas. These multiple states of matter occur when a substance is heated to temperatures above the binding energies for the different states of matter (solid, liquid, gas) to the point where the substance undergoes one or more phase transitions. This is one of the remarkable attributes of plasmas. They can be scaled insofar as the same qualitative properties can occur in plasmas differing by many orders of magnitude. For example, water ( $H_2O$ ) is in a crystalline (ice) and solid form as an exemplified first state of matter, a strongly-coupled medium (the binding energy is large compared to thermal energy) when it is below 273 K (0.0 Celsius). When the temperature of water is between 273 K and 373 K, the coupled crystalline bonds become disassociated. However, large molecular-size structures still exist and create the second state of matter for water, a liquid which is also a medium with strongly coupled bonds. When temperatures are raised to levels above 373 K (100 Celsius), the structural molecular bonds are disassociated and the water molecules form a gas which is known to be steam, its third state of matter. If this steam is heated further to a temperature where the binding energy of the water molecules reaches approximately 0.3 electron volts, its molecules further dissociate into separate hydrogen and oxygen atoms. Although this

state of matter for water is no longer steam, it is still a gas whereby the hydrogen and oxygen species are electrically neutral. This third state of matter then becomes a neutral gas which is no longer strongly coupled as a medium. The fourth state of matter is finally achieved with water when the gas is heated to the point where a large proportion of the water's atomic bonds are completely dissociated into negatively charged electrons and positively charged ions. An ionized gas is therefore formed. The proportion of atoms that become dissociated describes the degree of gas ionization. As temperature is increased, collisions between atoms increase and create greater (if not complete) ionization within the medium. This ionized gas medium achieves a plasma state where a multitude of charged particles interact within an electromagnetic field. If this plasma gas medium were to be heated further, the collective particles within the plasma would break apart nuclear and quark bonds to form another form of plasma beyond the scope of this work.

To explain in further depth what is defined as an ionized gas, there are significant numbers of unbound (free) electrons and electrically charged ions with neutral atoms and molecules which are normally resident in a gas. It is important to note that although these electrons are unbound, they are not "free." Rather, when the charges move they generate electrical currents with magnetic fields. As a result, they are affected by each other's magnetic fields. This ultimately governs their collective behavior. When the gas is neutral, two-particle (binary) collisions are the predominant particle interactions. Plasmas resulting from ionization of neutral gases generally contain equal numbers of positive and negative charge carriers. But again, when a plasma is formed by ionizing the gas, the charged particles will interact with other charged particles in the plasma in a collective manner. The behaviors of plasmas are therefore determined by the inherently weak interactions between the charged particles within it. The charged particles within plasmas interact collectively within the confines of the plasma's electromagnetic fields. Coulomb's law states that "the magnitude of the electrostatic force of interaction between two point charges is directly proportional to the scalar multiplication of the magnitudes of charges and inversely proportional to the square of the distances between them." Many charged particles interact simultaneously in these collective interactions because the Coulomb electrostatic force induced by each charged particle is a force that decreases as the reciprocal of the square of the distance from the charged particle.

Therefore, a charged particle will encounter the electrostatic forces from nearby charged particles. This interaction is collective because the nearby particles also react to the electrostatic forces from all the other nearby charged particles. Hence, a plasma can be described as a highly active ionizing and polarizing medium.

The motion of charged plasma particles has been the subject of much recent research. For plasmas which are not magnetized, the motion of these particles is literally and figuratively “straight-forward” insofar as the constituent particles basically move in straight lines between collisions. In a magnetized plasma, particles are scattered after executing a very small path along what is known as a “gyro (circular) orbit.” As such, these particles will still move in straight lines between collisions. More curious are what are known as “collisionless” magnetized plasmas where particles move perpendicular to magnetic field lines, as well as parallel to the field-lines. Since most of these collisionless magnetized plasmas occur in nature, space, and astrophysical plasmas, they will not be explored within the scope of this writing.

Plasmas are without question chemically active mediums. There are a number of methods to activate plasmas and their capacity to modify surfaces, for example. The methodologies by which they are employed can either generate low temperature (cold) plasmas or a very high temperature (thermal) plasmas. This wide variation in temperature range allows plasma technologies to be employed with a number of applications, such as surface modification, surface depositions (coating), destruction of solid wastes, air purification, surface sterilization, and many others. The industrialization of many of these process applications is expanding rapidly. This is partially due to the fact that plasmas can offer a highly sustainable alternative to most chemically aggressive alternatives which are becoming increasingly unsustainable due to environmental implications. More specifically, thermal plasmas offer unique advantages for the processing of materials, such as high fluxes of heat and reactant species. More recent developments have included improved control of these fluxes across the boundaries surrounding thermal plasmas. Practical applications of cold plasmas have been developed in the microelectronics industry, but the use of vacuum plasma equipment limits their utilization where high throughput is desired. This is where atmospheric cold plasma technologies are now beginning to be implanted. For reference, plasmas which have temperatures below about 100 electron volts (eV) are considered

“cold,” while those plasmas with temperatures ranging from 100 eV to 30 kiloelectron volts (keV) are generally considered “hot.” Energetic particles with high energies, like those that are found in the radiation belt, are termed “energetic.” These cold and thermal plasmas will be discussed in greater detail in the next section.

Surface-modifying plasmas generated by electromagnetic fields are typically identified as an electrical discharge. This type of plasma will typically employ diffused gases to create a gas phase, or gas discharge, plasma which is characterized as a partially ionized gas containing neutral particles and an equal number of negative electrons and positive ions. More precisely, when an electromagnetic field is applied to a gas, free electrons will be accelerated and gain kinetic energy. When a highly energized electron collides with a neutral molecule, the molecule can ionize by either losing an electron or accepting an electron. If an electron is lost, the newly released electron quickly experiences the electrical field and gains energy. This process is described as an “avalanche” which results in an intensive quasi-neutral cloud of electrons, ions, and neutrals in a constant agitation, as long as the electrical field is active. By modifying key parameters such as high frequency power levels, plasma chamber pressure, gas mixtures, gas flow rates, and dwell (exposure) time, a prescribed plasma chemistry can introduce useful changes to a substrate surface. These changes can be magnified when completely ionized gas phase plasmas are formed at both low and high pressures and densities where all particles are ionized, and also with negative ion plasmas.

## 1.2 Thermal vs. Nonthermal Plasmas

Generally speaking, plasmas can be delineated into two main categories, high temperature (fusion-type) plasmas and low temperature plasmas which are inclusive of gas discharges. If a plasma is considered high temperature, it is understood that its active species (electrons, ions, neutrals) are in a state of thermal equilibrium. It is important to note that low temperature plasmas can be further delineated into thermal plasmas, also known in the literature as quasi-equilibrium plasmas, which are in a state known as a local thermal equilibrium state (LTE), and nonthermal plasmas (NTP), which are also called nonequilibrium plasmas or cold plasmas. Below is an in-depth analysis of these plasmas, and how they contribute to surface modification.

### 1.2.1 Thermal Plasmas

Thermal plasmas (TP) are typically characterized by having an equilibrium state, or very near equilibrium, between electrons, ions and neutrals within the plasma. Some of the more common thermal plasmas used for practical application of these plasmas are plasma torches and microwave-based systems. From an applications standpoint, these system types produce high heat fluxes for use in processing plasma materials and for sterilization of waste materials. Regarding the latter, high temperature thermal plasmas are suited for processing the solid wastes of municipalities, highly toxic wastes, medical disposables, hazardous industrial wastes, and even the reduction of nuclear wastes. However, the application of thermal plasmas may not necessarily be acceptable for certain waste disposals and reductions for a number of reasons, including safety relative to reaction by products. In these cases, a more suitable technology can be cold gas-phase discharges. We will explore this technology later on in this work.

Thermal plasmas can be distinguished from many other types of plasmas by their very unique physical properties. Here are some of these defining properties:

- Thermal plasmas, such as an argon gas plasma DC plasma torch, can register temperatures in the vicinity of 11200 K.
- Their species have Maxwellian velocity distribution, or particle speeds where the particles do not constantly interact with each other but move freely between short collisions. This property describes the probability of a particle's speed (the magnitude of its velocity vector) being near a given value as a function of the temperature of the system, the mass of the particle, and that speed value. If these particles have the same temperature, they are understood to be in local thermodynamic equilibrium (mentioned above).
- When the energy states of particle species are at a density to a "Boltzmann" term, particle species can collide and produce different species. This is how the formation of the light elements in big bang nuclear synthesis is calculated.

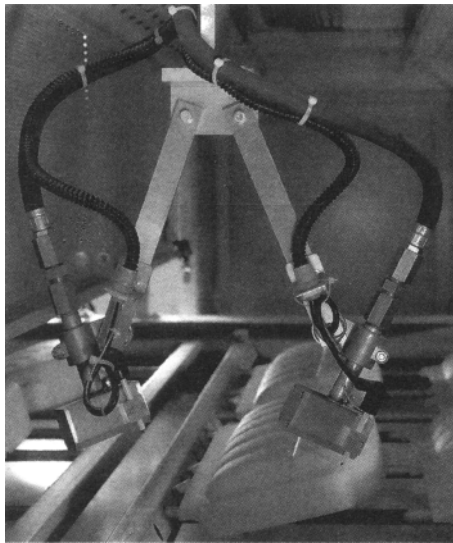
- The physical composition of thermal plasmas can be determined from a state of local chemical equilibrium (LCE).
- Thermal plasmas are not typically restricted by electromagnetic fields.
- Thermal plasmas are able to be stabilized by physical barriers such as walls, by high velocity gas flow rates, and by the discharge profile of their electrode discharge mechanisms.

As alluded to previously, thermal plasmas can be created by direct current or radio frequency arcs, for example, or by an inductively-coupled torch, or plasma (ICP). Direct current (DC) plasmas operate from having a sufficient supply of electrons at the cathode electrode. With a plasma developed from an arc discharge, the supply of electrons is produced by raising the temperature of the cathode to the point where the emission of thermal ions is a high velocity. At this state, there can be a degradation of the physical cathode material by thermal erosion and evaporation. This is most commonly exemplified in arc plasma welding, where the electrode material ultimately becomes the weld. ICP torch systems are designed to generate a plasma with a gas (other gases) in which the atoms present in an ionized state. The basic construction of an ICP typically consists of three cylindrical tubes made of silica a few centimeters in diameter. These tubes, termed an outer loop, an intermediate loop, and an inner loop, collectively make up the torch of the ICP. The torch is contained within a water-cooled coil (2–5 turns) of a radio frequency (RF) generator with power capacities ranging from 1 kW to 15 kW and gas flow rates within the tube from 1–30 slpm. A separate cooling method is typically incorporated within the tube to guard against excessive heating. As flowing gases are introduced into the torch, the RF field is activated and the gas in the coil region becomes electrically conductive. This sequence of events forms the plasma. From a surface modification standpoint, these plasmas can be applied to rapidly remove photoresists from within circuit board manufacturing processes (oxygen-based thermal plasmas), and within silicon wafer processes.

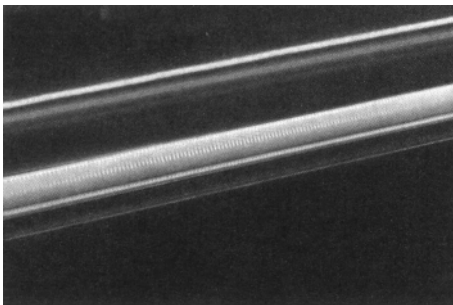
Local thermal equilibrium states within thermal plasmas are not prevalent states. Rather, complete thermal equilibrium can usually not be achieved for multiple ionized species. Among the various



methods of plasma diagnosis, such as with spectral analyses using microwaves, lasers, and magnetics, diagnosis based upon their own radiative techniques involves losses of radiation by plasma. As such, thermodynamic equilibrium cannot be fully achieved. As such, the excited state of thermal plasma species typically will not align with Boltzmann equilibrium. Also, only partial local thermal equilibrium (known as pLTE) can describe such a state. Factors such as pressure, electron density, and temperature become the key plasma parameters. Here are characterizations of pLTE:



**Figure 1.1** Enercon flame plasma for three-dimensional objects.



**Figure 1.2** Enercon flame plasma for webs.

## 10 ATMOSPHERIC PRESSURE PLASMA FOR SURFACE MODIFICATION

- The proportion of excited states to the total plasma's thermodynamic potential is very small.
- Electron temperature and gas properties mainly determine the plasma's physical composition.
- Heating, radiation, and other thermal transfer properties define the energy balance of the thermal discharge.
- High density gas-phase (arc) discharges in atmosphere are modified by natural heat transfer.
- Arc discharges initiated the development of plasma physics.
- Excited-state plasma species do not directly impact arc discharge properties.

Discharge powers for pLTE thermal/arc plasmas can range from watt to megawatts, with most discharges taking place under atmospheric plasma conditions. Models of stationary arc discharges are wide-ranging and include the following:

- Arc welding devices
  - Unsteady, three-dimensional thermal plasma flow
  - Arc configuration optimization improves performance
  - Gas mixtures and flow rates, along with electrode material type can provide predictive results.
- Plasma torch devices
  - Ionized gas that conducts electricity
  - Controlled plasma generated from steady gas flow ( $N_2$ ,  $O_2$ , or air) between electrodes
  - Average temperature around 6,000 Celsius
  - Applied for waste destruction
  - Applied in space propulsion
  - Will synthesize nanomaterials
  - Deposition of chemistry and performance materials, such as by plasma spraying of ceramics, and the removal of surface layers, such as by plasma etching.
- AC or DC arc lamps
  - Consist of two electrodes, typically made of tungsten, which are separated by a gas.
  - Gases used include neon, argon, xenon, krypton, sodium, metal halide, and mercury.

- High voltage is pulsed across the lamp to “ignite” or “strike” the arc across the gas.
- Performance is dependent upon electrode geometry.
- Have electrical characteristics which change with temperature and time.
- Have applications such as cinema projection and searchlights
- Arc furnaces
  - Heat charged material by means of an electric arc.
  - Industrial electric arc furnace temperatures can be up to 1,800 degrees Celsius.
  - Charge material is directly exposed to an electric arc, and the current in furnace terminals passes through the charged material.
  - Allows steel to be made from a 100% scrap metal feedstock.
  - Can replace carbon electrode technology.

Applications of thermal plasmas have needed to address several issues, including arc stability and use of specific gases. Configuration modifications have included injections between three cathodes and one anode (with and without separate arcs), and into plasma jets downstream of the anode. Still others have used modified plasma torches with shrouded gas discharges to improve fluid dynamic performance. The use of RF plasma spraying techniques which incorporate different nozzle designs to increase the velocity of plasma jet particle velocity have also been evaluated to approximate the performances of DC plasma spraying technologies while retaining injection and dwell time advantages of radio frequency processes. This is most notably represented by the development of what are known as suspension plasma spraying techniques whereby precursor to be deposited, typically a ceramic feedstock, is dispersed in a liquid suspension before being injected into the plasma jet. With the suspending powder localized in a fluid, normal feeding problems are circumvented allowing the deposition of finer microstructures through the use of finer powders. Other techniques include the use of hybrid plasma torches which utilize the advantages of DC and RF plasma spraying techniques. A DC-RF hybrid plasma torch has a very complex flow discharge structure because of the interaction between a DC plasma jet and the RF flow. As a result, flow control of a DC-RF hybrid plasma is

critical, necessitating the need for separate power supplies and controls to enhance its characteristics related to flow temperature, flow stability and the length of the plasma discharge flame.

There has also been a great deal of new process control innovation related to the development of thermal plasma operational diagnostics to monitor and control flows. Specifically, the measurement of spray particle temperatures and particle velocities that allow for adjustment and optimization of these parameters. There are also sensor measurements of discharge sound frequency and changes in voltage in order to improve discharge integrity and reliability.

Another area of development is with the use of thermal plasma CVD (chemical vapor deposition) whereby the plasma discharge is the "manufacturing zone" of desired chemical radicals which are intended to modify the interfacial surface to which it is driven. One application involves the synthesis of diamond crystals and films by use of DC thermal plasma jet CVD at a pressure of one atmosphere. Such a design can involve a multiple torch plasma reactor to generate a convergent plasma jet to entrain participating gases. The multiple coalescing plasma jets produced by this reactor direct the dissociated and ionized gaseous species onto silicon wafer substrates where the diamond can grow. A key advantage of using a thermal plasma CVD process is the high precursor deposition rates associated with the process, and the large range of reactive precursors which can be used. The inflight time of precursors between injection and substrate application is typically less than 1ms. Process control is also critical here to ensure that deposition thickness and precursor concentration level is uniform as the plasma penetrates the surface boundary layer. This has more recently been accomplished by using a lower velocity DC glow discharge plasma jet at atmospheric pressure.

There are methodologies other than thermal plasma chemical vapor deposition which can be used to generate and deliver reactive species at high velocity to a surface. These incorporate designs based upon fluid dynamics to maintain high species concentrations while they are in flight to the base substrate. A practical example of such a design is the caliper reduction of silicon wafers by aggressive chemical surface etching under low pressure. There are also the sterilization of food and food packaging under both low and high pressure discharge environments. One such applicable device design involves a linear plasma jet

generated by the ionization of a reactive gas pressured through an electrical arc which is partially stabilized by magnetic fields. This type of device can be efficient and economical if the discharge is generated at atmospheric pressure and in the regimes of dielectric barrier discharges or glow discharges, so as to significantly reduce heat generation.

More recently, thermal plasmas have been used to synthesize nanoparticles. These nanoparticles are nanophase materials (under 100 nanometers) which have different mechanical and optical properties compared to the large-grained materials of the same chemical composition. The extremely high particle generation and reactive precursor flow rates created by thermal plasmas can effectively reduce processing time from precursor injection to nucleation to less than one millisecond. The bulk fabrication of nanoparticles with key functional properties has been realized by use of hypersonic plasma particle deposition (HPPD), wherein a thermal plasma seeded with vapor-phase precursors (reactant) is supersonically expanded through a nozzle to nucleate ultrafine particles which are then deposited by hypersonic impaction onto a temperature-controlled substrate. Cooling of the precursors by expansion leads to particle formation in the range of 10–20 nm. Examples of properties created by synthesis of nanoparticles by thermal plasmas include greater strength, hardness, ductility, sinterability, greater reactivity, and many others.

Plasma waste treatment has become a more prominent technology of late because of the increasing problems with waste disposal, and because of the many potential processing by products. Large volume reduction of hazardous wastes using thermal plasma processes is increasingly becoming more prevalent. The advantages of using thermal plasmas for waste treatment include high heating temperatures and low gas byproduct flow rates. The process is also known as thermal plasma pyrolysis whereby a carbonaceous solid is reacted with oxygen at high temperature to produce solid and gas by products. Not unlike other plasmas, the plasma itself is composed of electrons, ions, radicals, and high energy UV radiation. When these carbonaceous particles are injected into a plasma, they are rapidly heated and create a gasification effect. By-products of this gasification reaction can include hydrogen, methane and acetylene. Regarding the economics of thermal plasma waste treatment processes, certainly the generation of combustible gases is just one example of a valuable byproduct.

### 1.2.2 Nonthermal Plasmas

A nonthermal plasma is generally a plasma discharge which is not in absolute thermodynamic equilibrium. This may be because the ionic and electron temperature vary from each other, or species within the plasma discharge have a velocity distribution which is not consistent with the distribution of velocities as defined and described as a Maxwell-Boltzmann distribution.

In the context of configuring a nonthermal plasma, a gas is initially diffused into a reaction zone. Under normal conditions, the gas acts as an electrical insulator. When a sufficient level of voltage is applied to a diffused gas (or gas mixture) within the treatment gap between the nonthermal plasma device and the substrate, the gas will breakdown and actively conduct electricity. The reason for this has to do with species polarity. The gas molecules or atoms are electrically neutral and are ionized by the electrical discharge, and therefore split up into negatively charged electrons and positively charged ions. Each gas composition will dictate the breakdown voltage required, and hence the ionization rate. Other manageable operating parameters such as gas flow rate and gas pressure, gas mixture percentage, substrate surface properties, the geometry of the surface, the distance (gap) between the discharge electrode and material surface across which the electrical potential difference is maintained, the distance between the anode and cathode electrodes, the design of the high voltage power supply, the design of the input transformer, and the design of the electrical circuitry will all impact the effectiveness of the nonthermal plasma discharge. The resulting ionized gas species are termed a discharge or plasma. The profile of these plasmas (e.g., glow, dielectric barrier discharge) can vary widely, but in general they all characteristically include partially ionized gases which will contain electrons, ions neutral atoms, and/or molecules. Uniquely, the interactions of these electrically-charged species with each other, along with neutral gases and with substrate surfaces will produce tailored physical and chemical modifications within the plasma itself. This changeable attribute of nonthermal plasmas is uniquely different from physical and chemical states found in solids, liquids or other gases. This has defined nonthermal plasmas as a fourth state of matter. However, revisiting the concept of momentum transfer between the electrons, gas molecules and ions in a nonthermal plasma is not completely efficient and so very often the energy residing within the plasma

more or less involves the electrons. As a consequence, ionized gases at low pressure and low particle densities are typically described as nonthermal plasmas. Translating, this means that the electrons, ions, and molecules within the ionized gas will be in thermal equilibrium and will only have the similarity of having species which have closely common atomic mass. And, as alluded to above, the velocity distribution of each particle or species can accurately be represented by a Maxwell-Boltzmann distribution and that temperature can represent overall energy distribution. It should be noted that electron temperature will most often be quite higher than the temperature of ions within the plasma and the temperature of the ionized gas.

Nonthermal plasmas have a wide range of applications. As an example, the processing of food by exposure to nonthermal plasmas can provide sanitizing surface effects. Further, the introduction of certain precursors can extend initial sanitation to antimicrobial treatments. Applications being investigated include the sanitizing of fruits and vegetable, as well as grains and other dry and wet foods. Objectives for introducing nonthermal plasmas for sanitation of these foods include the potential elimination of harmful pesticides and for energy conservation relative to the use of sanitizing levels of heat.

In the realm of nonthermal plasma descriptors, the term “cold plasma” has been used to distinguish these atmospheric pressure, ambient temperature plasma discharges from those which operate at several hundreds or several thousands of degrees (Fahrenheit) above nonthermal plasma discharges. Considering again applications within food processing, it can therefore be understood as to why such cold plasma regimes are more readily perceived and accepted as an alternative to “hot plasma” and other quality-endangering methodologies.

Descriptors of nonthermal plasmas typically found within technical literature vary considerably. Most of this variability in description is derived from phraseology used to describe its mechanical construction or discharge profile. Examples of these include “plasma jet,” seeming to promise a high velocity torch-like discharge. Another is “plasma pencil,” indicating a fine or pin-point plasma discharge. There are also more descriptive phrases used, such as “dielectric barrier discharge,” “atmospheric plasma,” “one atmosphere plasma,” “glow discharge plasma,” “nonthermal atmospheric plasma,” and “non-equilibrium ambient temperature plasma” to name only a few

which tend to define the principle and/or the physical/electrical characteristics of the plasma. To effectively navigate through these descriptors, one must understand the primary features of nonthermal plasmas which distinguish them from those plasmas which have been developed and applied within industrial settings. These features are 1) that the plasma is indeed nonthermal, and 2) that the plasma operates at atmospheric pressure.

Stepping back briefly in history, low pressure vacuum technology must be recognized as the genesis of nonthermal plasma technologies used today. The low pressure plasmas became established in industry around the year 1900 for use in manufacturing electric light bulbs. Many other electronic devices which required a low pressure vacuum for operation soon followed, such as variations in the electron tube. Later, it was discovered that particular processes conducted in a vacuum revealed results superior to any available technique under atmospheric conditions. These processes include the coating of the surface of lens to modify light transmission, the conditioning of blood plasma for blood banks, and the complex process of producing titanium. In the 1950s, large scale development of vacuum plasma technologies evolved with the advent of nuclear power generation. And in the decades to follow, vacuum plasmas enabled simulation technology for aerospace, and for the fabrication of microelectronics.

Today, industrial-scale vacuum applications can range from simple material handling technologies such as suction devices to complex depositions of IECs (integrated electronic circuits) on silicon-based chips. To categorize these applications, vacuum pressures from one torr (approximately 133.32 pascals, or 1/760 of atmospheric pressure) to near atmospheric pressure include the aforementioned mechanical material handling applications, the forming of vacuum-based packaging, the sampling of gases, the filtration of various mediums, oil degassing, water-based solution concentration, the impregnating of electrical parts, and the degassing of metals such as steel and aluminum. For dry plasma etching processes for silicon wafers (between 0.1 and 5 torr), vacuum plasmas produce free radicals, neutrally charged, that react at the surface of the wafer. Since neutral particles attack the wafer from all angles, this process is isotropic.

Progressing down the pressure scale to about  $10^{-4}$  torr, additional metal process-related applications benefit from vacuum plasma. These include the melting and casting of metals, tempering/heat treatment processes, and metal sintering by spark plasma sintering (SPS) or pulsed electric current sintering (PECS).



Also required in this pressure range are processes such as vacuum distillation, whereby materials such as platinum and lead can be separated at high temperature because of their different vapor pressures. The freeze-drying process also requires this vacuum range and is used for preparing pharmaceuticals. By removing water from materials and sealing material in vials, materials can be easily stored, shipped, and later reconstituted to their original form for injection. Another example from the pharmaceutical industry is the use of freeze-drying to produce tablets or wafers, the advantage of which is a rapidly absorbed and easily administered dosage form. Freeze-drying is also used to store skin and blood plasma.

Between  $10^{-6}$  torr and  $10^{-4}$  torr, vacuum plasmas have evolved from producing picture tubes for television sets and medical X-ray tubes to thin film coatings for optical, electrical and protective/decorative applications. For thin film applications, metals such as aluminum, titanium, tungsten, or compounds are evaporated within the vacuum chamber onto a wide range of base substrates such as plastics, glass, ceramics, and silica. The thickness of these coatings can range from a few atomic layers to 10 microns or more. Considering optical depositions, special antireflection coatings are applied to enhance the performance of telescopic devices, cameras, and other lenses to reduce the amount of lights which may otherwise be reflected by the lens in order to improve the brightness of the transmitted image.

Vacuum deposition at high frequencies enables very short deposition times and high deposition rates, and both are needed to produce, for example, extremely high-quality microcrystalline silicon layers for industrial applications. This type of high frequency plasma-enhanced chemical vapor deposition chamber contributes to the ability to study the effects on product performances such as solar cells. This particular application deposits hydrogenated amorphous silicon (a-Si:H) and microcrystalline silicon ( $\mu$ c-Si:H) layers. Material temperatures can range up to  $400^{\circ}\text{C}$  at frequencies up to 100 MHz at  $10^{-8}$  torr (ultra-high vacuum). Typical flow gases can include Ar,  $\text{SiH}_4$ ,  $\text{H}_2$ , and  $\text{SiD}_4$ .

Although low-pressure (vacuum) glow discharge plasmas offer advantages in analyses, research, and in material sciences, microelectronics, and solar commercial applications to name a few, these plasmas must be contained within capital-intensive, airtight and quite large vacuum reactors. Not only are these systems expensive to acquire and operate, the process requirements of batching

materials within the chamber, the time requirement of pumping down the vacuum, applying the required treatment reaction time, and then returning the chamber to atmospheric pressure is an unavoidable routine. In addition, the density of reacted particles within the plasma is relatively low and therefore requires extended dwell or exposure times. As such, there has been concerted efforts to develop plasma sources which are not only operable at atmospheric pressure but also deliver the modification effects of low pressure vacuum regimes. The attractive economical advantages of operating at atmospheric pressure have led to the development of a wide range of industrial, scientific and academic nonthermal plasma sources. These atmospheric nonthermal plasmas are being formed by a diverse range of discharge profiles, including corona discharge, dielectric barrier discharge, gliding arc, hollow cathode discharge, blown arc, blown ion, and atmospheric plasma jet.

The initial type of regime developed to generate an atmospheric nonthermal plasma was the corona discharge. The field polarity and the geometric configuration of the electrode (or electrode set) defines the form of corona discharge. A corona discharge is characterized by symmetrical electrode bars, and its discharge results from an electromagnetic field which surrounds the electrode configuration. The electrodes are energized with a pulsed or continuous AC or DC voltage. Within what is typically a non-uniform electromagnetic field between the electrode pair and the air gap to a substrate surface, the electrical field in close proximity to the

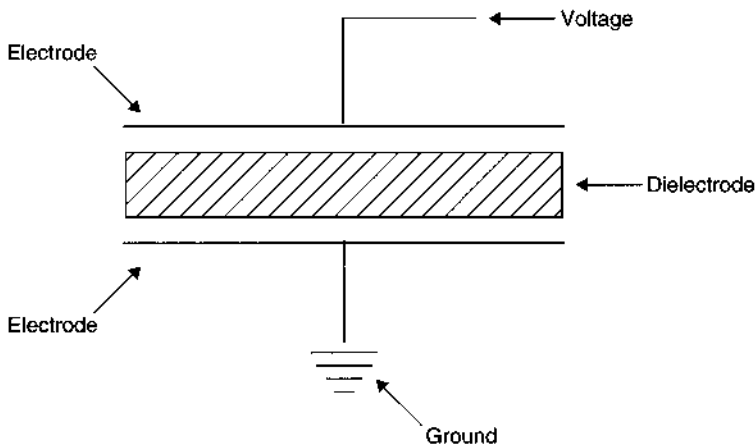
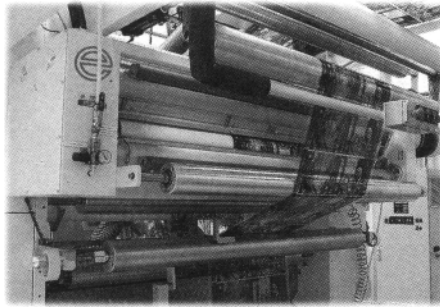


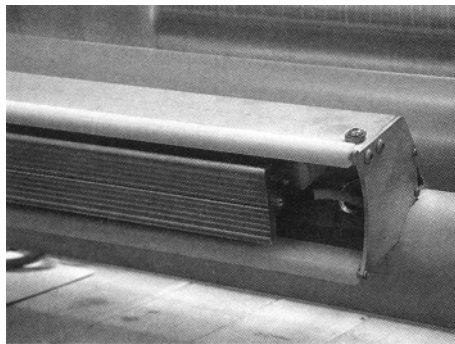
Figure 1.3 Dielectric barrier corona discharge.



**Figure 1.4** Enercon universal corona discharge system.



**Figure 1.5** Ceramic corona discharge electrodes.



**Figure 1.6** Metal "shoe-type" corona discharge electrode.

electrode pair becomes stronger than the breakdown voltage of the air in the air gap. Ultimately, a non-uniform and weakly ionized nonthermal corona discharge is generated.

Although corona discharges are characteristically non-uniform discharges, they can also be described either as "positive coronas,"

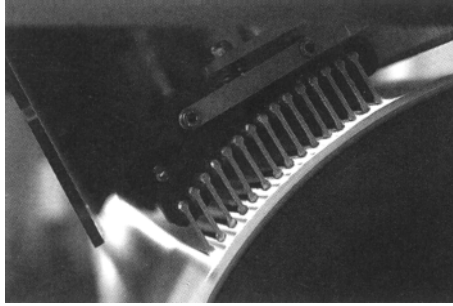


Figure 1.7 Metal “fin-type” corona discharge electrode.

when the electrode with the most curvature is connected to the positive terminal of power supply, and “negative coronas” when this same electrode is connected to the negative terminal of power supply. A corona discharge develops by following a defined progressive sequence whereby 1) high voltage is applied to an electrode, 2) an electron avalanche begins building, 3) photons emanating from the avalanche create new charges, and 4) an avalanche also begins developing from the opposite electrode. This progression is commercially beneficial within corona surface treating technologies used for polarizing flexible roll-to-roll materials, electrostatic precipitators used for dust collection devices, ozone generation systems for water purification and extrusion coating applications, copy machines, powder coating processes, and others.

Other atmospheric pressure nonthermal plasma technologies include blown arc, blown ion and other plasma jet-type constructions. These devices typically consist of two opposing electrodes through which either air or gas mixtures of helium, argon, nitrogen, carbon dioxide or oxygen flow. In this design configuration, one electrode is coupled to low-to-high frequency power ranging from 30 kHz to 13.56 MHz at voltages between 100 V to 250 V, and the other electrode is grounded. Once radio frequency power is applied, the discharge becomes ignited and partially ionizes the mixture gases which have their flow rates controlled either by valves, rotometers or electronic flow meters. The gases flow between the opposing electrodes to produce a high velocity flow of reactive chemical species. In principle, electrical power energizes and accelerates free electrons which collide with the feed gas to produce free radicals, excited molecules, excited atomic species, and pairings of ions and electrons. As the feed gas leaves the discharge device,

reaction-forming electrons and ions recombine. But the partially ionized, high velocity discharge stream still harbors free radicals and neutral metastables. As a result, these atmospheric pressure nonthermal plasma technologies produce homogenous and uniform discharges at low to high frequencies. Additionally, these discharges are relatively free of arcs (also known as streamers or filaments) when directed to a substrate. The feed gas temperature of these discharges can be below 50°C or greater than 300°C to functionalize temperature-sensitive materials or clean high density materials, respectively, without creating surface damage. Key substrate processing applications include surface etching of metals and polymers, as well as the deposition of silicon dioxide (SiO<sub>2</sub>) on surfaces by chemical vapor deposition techniques to create anti-reflective surface properties, for example. These devices can also provide surface decontamination of surfaces debased by biological and chemical agents, and remove atomic species with unstable nuclei from surfaces. They are also useful as ecological techniques for volatilizing organic contaminations from metal surfaces as opposed to the use of chemical surfactants and solvents, for sterilizing medical devices and surfaces, and for functionalizing narrow width two-dimensional spool-based materials.

Another design of atmospheric pressure nonthermal plasmas is that which is based upon microhollow cathode discharge (MHCD) electrode technology. Microhollow cathode discharge devices have attracted much attention because they can be operated at atmospheric pressures. These designs consist of a metal-based cathode with a hole in the center and a metal-based anode, both being separated by an insulator. Conceptually, different cathode shapes can create an increase in current density relative to a linear discharge. The generation of electrons in hollow cathode discharges is caused primarily by emissions of secondary electrons as a result of bombardment of the cathode by metastables, ions and photons. Typical hole diameters for atmospheric pressure discharges in microhollow cathodes are measured in micrometers. To further characterize MHCDs, they are operable in either pulse or DC modes, and have parallel electrodes separated with dielectric coatings. Microdischarges generated by MHCDs offer low cost operation, due to their small size and low power consumption. Therefore they are attractive for plasma applications in industry for surface treatment, generation of UV and VUV radiation, reduction of pollutants, gas lasers, biological decontamination, and thin film deposition, mainly in a high pressure operation.

Finally, dielectric barrier discharges (DBDs) constitute yet another nonthermal, AC-based plasma generated at atmospheric pressure. This non-equilibrium plasma operates at low gas temperature and is typically generated with two electrodes, one or both of which are insulated to provide optimizing dielectric properties, in order to eliminate electrode deterioration. Electrically, DBDs utilize AC voltage which generally ranges up to 10 kV in amplitude, and frequencies ranging from lower RF to microwave frequencies. Many random arcs form between the two electrodes during operation. As charges accumulate on the surface of the dielectric covering, they ultimately discharge in microseconds. These plasmas are sustained when the power source continues to supply enough energy to sustain gas ionization. The DBD discharge process initiates the emission of photons with an energy and frequency directly relative to the gas employed within the discharge (or treatment) gap.

More specifically, DBD discharges can be manufactured in many configurations. Typical designs are planar, using parallel plates or bars separated by one or two dielectric barriers located either on the high voltage or grounded electrode, or on both the electrodes, or between two metal electrodes. With coaxial designs, one electrode is constructed inside another with dielectric barrier positioned between them. Coaxial designs are filled at atmospheric pressure with a rare gas or rare gas mixture. Dielectrics employed within these designs include glass, ceramics and quartz. These designs are used for energizing plasma displays, generating ozone and powering lasers. The gas ionization gap ranges between 0.1 mm to 30 mm. The two primary DBD discharge types are those which have filament-based (canal-type microdischarges) with random avalanches from electrode surfaces, and glow discharges which are nearly non-filamentary and homogenous.

### 1.3 Mechanisms for Surfaces Reactions

There are two primary mechanisms for surface reactions by plasma processing methods. One is a physical reaction mechanism which is performed by ionic activity. The other is a chemical reaction mechanism created by free radicals. With physical reactions, ionic species obtain charge and kinetic energy from a powered electrical field generated from an electrode. Molecules and atoms (and any trace contaminants) are dislodged from targeted surfaces as energy



Table 1.1 Selection of surface activation effects by plasma system type.

Mode of Species Excitation	Plasma Type	Plasma Gas	Base Substrate	Activation Effect
Radio Frequency	AP Jets / Roll-to-Roll / Planar	He/O <sub>2</sub>	ETFE	Wettability > 42 mN/m, Defluorination, High Uniformity
Low Frequency	AP DBD Systems	He/O <sub>2</sub>	Polypropylene	Wettability > 44 mN/m, High Uniformity
Pulsed Direct Current	Corona Discharge, Glow DBD	Air, He/O <sub>2</sub>	Polyethylene	Wettability > 42 mN/m, High Oxygen Atom Density
Pulsed Alternative Current	Corona Discharge, Glow DBD	Air, He/O <sub>2</sub>	Polyurethane	Wettability > 46 mN/m, High Oxygen Atom Density



films which will have control of thicknesses at the atomic level. This deposition technique establishes its control of conformal film growth by alternating, as a reaction mechanism, adsorption to ensure that a monolayer of conformal film is deposited. Selection of the number of deposition cycles will control the film thickness. A gas-phase plasma can be used to activate a reactant to increase reactive mechanisms within a substrate's surface chemistry.

To understand the mechanisms for surface reactions which take place in a gas-phase plasma atomic layer deposition, one need only review the deposition of species such as metal oxides or nitrides. Metal oxides, for example, will deliver high quality conformal films with the particular assistance of oxygen-based plasmas [8]. In addition, the growth of aluminum oxide will take place as a result of a carbon/hydrogen-like, surface-resident chemistry. Increasing surface exposure to a plasma can help to improve conformal film quality, as well as the properties of the film.

Another approach for understanding plasma-based surface reaction mechanisms is to consider plasma-enhanced chemical vapor depositions (PECVDs). Desired surface properties created by the deposition of amorphous hydrogenated silicon films, for example, can be achieved when there is a complete understanding of surface reaction mechanisms during this process. Plasma discharges with silane gas chemistry will develop  $\text{SiH}_x$  radical interactions at surfaces exposed to this discharge, as well as break surface molecular bonds, which ultimately determines chemical reactivity. In practice, high levels of hydrogen atoms at a substrate surface exposed to a silane plasma will enhance the reactivity of  $\text{SiH}_x$  radicals and reaction mechanisms at the plasma-exposed surface.

