# PLASMA SCIENCE AND TECHNOLOGY

**J. Leon Shohet**
*University of Wisconsin-Madison, USA*

**Keywords:** plasma, diffusion, transport, probes, glow, arc, potential, conductivity, deposition, etching, microelectromechanical systems, biomaterials, polymerization

## Contents



## Summary

The plasma state of matter can be considered primarily as a miniature chemical reactor, and some chemical reactions can only take place under such conditions. As a result, a unique opportunity exits for developing materials that are precisely tailored for use in the life sciences. In order to use plasma treatments properly, it is necessary to understand their properties, production, and use, and their interaction with materials. Basic plasma properties are described, including density, temperature, and composition, while at the same time the dynamics of such plasmas are considered so that particle and heat transport, and species concentration, can be calculated and measured. Key plasma-surface interactions are described, such as deposition, sputtering, etching, and implantation, along with types of chemical reactions in the plasma state as well as on surfaces immersed in the plasma that are of interest to the life sciences. Finally, some examples and descriptions of plasma-produced biomaterials and biomicroelectromechanical devices are provided.

## 1. Introduction

Plasmas are composed of mixtures of electrons and positive and/or negatively charged ions, as well as neutral particles. They are affected by electric and magnetic fields, which can be used to modify their properties. The temperature of such plasmas can be quite high. As a result, many interactions between particles are substantially different when they are in the plasma state. Thus, new materials can be manufactured that can have improved properties, new chemical compounds may be produced, and the surfaces of existing materials can be altered. These aspects will have an increasingly significant role in the future of technology, especially as applied to the life sciences.
In the past, most applications of plasma technology to the life sciences treated plasma as a "black box" in which little if anything was known about its properties. At present, industrial plasma applications are largely empirical in nature. Further progress will require a much more thorough understanding of plasma behavior, as well as of the interaction of plasma with solid materials. Design tools, transportable diagnostics, and models are needed. It is one of the goals of this article to provide workers in the life sciences with a basic understanding of the physical and chemical properties of plasmas that have the potential to make them so useful in this area.

The use of plasma technology has applications that cover a broad range of activities and has a multibillion-dollar yearly impact in the economy. In order to understand how this occurs, we must first describe what a plasma is, how it behaves under the influence of electric and magnetic fields, and how it is characterized. Normally, we specify the following quantities when we describe plasma's composition: electron and ion temperatures, and electron and ion densities. We divide plasmas into two general types as follows:

1. *Industrial plasmas.* The ions in these plasmas are generally composed of masses above hydrogen (the molecular weights can reach several thousand), and are usually of two types: thermal (equilibrium) plasmas, in which the electron and ion temperatures are approximately equal, and nonequilibrium (glow-discharge) plasmas, which tend to have relatively high electron temperatures compared to the ion temperatures.
2. *Fusion plasmas.* These plasmas have much higher temperatures than industrial plasmas, are composed of light atoms—particularly hydrogen or its isotopes—and

are designed to produce energy by means of a thermonuclear reaction.

We characterize industrial applications in three broad and somewhat overlapping areas. They are:

1. Plasma processing, which encompasses applications in which plasmas or particle beams—charged or neutral—are used to alter an existing material, as in plasma etching, ion milling, ion implantation, or surface modification through plasma cleaning, hardening, or nitriding.
2. Plasma synthesis, which refers to applications in which plasmas are used to drive or assist chemical reactions to synthesize compounds, alloys, polymers, or other complex species starting from simpler starting materials. This could also include the inverse processes of plasma decomposition. Many chemicals and/or chemical reactions can only exist or take place in the plasma state.
3. Plasma electronics, which includes applications in which the unique properties of plasmas are used directly in devices, such as arc melters, microwave sources, switchgear, plasma displays, welders, analytical instrumentation, arc lamps, or laser tubes.

There are four common fundamental requirements needed for progress in applications of plasmas. They are:

1. Theory, modeling, and systems concepts.
2. Plasma chemistry and interactions.
3. Plasma diagnostics and characterization.
4. Plasma generation and confinement.

It is the purpose of this article to provide a general introduction to plasma science and engineering in order to show both the applications and how advances in this field can be made. The following short description of industrial applications of plasma processing and technology shows how widespread the impact of plasma technology is.

**Plasma polymerization.** By ionizing a monomer gas, certain types of polymers can be made that can be deposited as coatings on various materials. There is an important application of this work in the biotechnology field, since biocompatible polymers can be used to coat various implant materials that would otherwise be rejected by the body and/or to provide a mechanism for drug delivery. Various pharmaceuticals and other "exotic" chemicals can only be made with this process, which is often a result of the combination of ion and free radical generation by the plasma. In addition, plasmas can activate, cross-link, or otherwise modify the structure of polymers, producing anti-adhesion, antifouling, or bacterial-resistant surfaces.

**Plasma-assisted CVD (chemical vapor deposition).** Here, plasmas can be used to provide a mechanism to successfully deposit various chemicals on surfaces, either by treating the surface before deposition or by providing a chemical pathway for successful deposition.

**Sputter deposition.** In this case, plasmas are used to sputter particles from a target electrode, which are then deposited on a particular material.

**Plasma etching.** The major applications of this work are in the semiconductor industry and for the fabrication of microelectromechanical systems (MEMS). As the spacing between lines in integrated circuits shrinks to 0.1 μ and below, conventional "wet" etching using chemicals begins to fail. This is because such processing acts in a spherical direction and undercuts the walls between the etch regions. Appropriately designed plasma etching (dry etching), perhaps combined with electric and magnetic fields or ion beams, offers a dramatic improvement in the etch process, and it is believed that the future of the entire microfabrication industry will continue to rest with plasma processing for a long time to come.

**Ion milling.** Beams of ions can be used to cut or "mill" narrow regions of materials to great accuracy.

**Surface modification.** Plasmas can be used to modify the properties of materials by interacting on the surface of those materials in several ways. For example, tool steel can be hardened considerably by subjecting the tools to a nitrogen plasma. Turbine blades can be plasma-coated for improved mechanical and thermal properties.

**Welding.** The use of plasmas in welding, especially in arc welding, has been known for some time. However, many problems continue to exist with welding, and much of it is because of the lack of understanding of the plasma composition, the plasma temperature and density, and the electric field and current distribution in the welding arc.

**Discharge machining.** In this process, plasmas are used to provide a cutting surface between a thin wire and the work to be cut, usually by passing an arc between them through water.

**Arc devices.** A major component of US industry has involved the use of arc technology in the electrical power system field. Switchgear today is still being designed empirically without the understanding of plasma-surface interactions. The US switchgear industry is suffering greatly from foreign competition as a result. Area illumination is a major application of this technology as well, with activity above US$20 billion per year.

**Arc melting.** Arc furnaces have been in use for many years. Their applications to the refining and extraction of ores have been many. Yet, major improvements can be made if the interactions of plasmas with ores and metals are properly understood. For example, in the melting of iron ore, 20 lb (9.07 kg) of graphite electrode are used up per ton of ore. If just 1 lb (0.45 kg) of graphite were saved per ton of iron ore, US$20 million per year savings would result.

**Plasma spray.** This is a coating process that sputters heavy particles (clumps) from the cathode of an arc system and then directs the spray of these particles to a surface for coating. It has applications where thick coatings are required.

Much needs to be done to formulate appropriate understanding of plasma and plasma-surface interactions. Measurements have often found that intuitive understandings of plasma behavior have not been borne out when the actual measurements are made. However, if the measurement system itself results in a perturbation of the plasma, the results may be unclear, and thus noninvasive diagnostics need to be developed.

## 2. Basic Plasma Properties

### 2.1. Density, Temperature, Composition

The mixture of ions, electrons, and neutral particles making up a plasma must be describable in terms of quantities that can be used to depict them so that their properties can be analyzed. There are several of these quantities that provide a useful comparison. They include:

- *Density*. Described by $n_e$, $n_{ix}$, and $n_x$, which refer to the electron density; the ion density of species, *x*; and the neutral density of species, x, respectively. It is important to note that most plasmas contain ions of several different species (positively and/or negatively charged), and the number density—usually expressed in units of particles per $cm^3$—is a very important quantity. The density is usually a function of both position and time.
- *Temperature*. Another important quantity that is needed to characterize a plasma is the temperature of the individual components (i.e., $T_e$, $T_{ix}$, and $T_s$). Temperature is also a quantity that is not usually constant in space or time, and is often measured in degrees kelvin or electron volts (1 eV = 11 600 K).

These two quantities should be measured experimentally and are then often modeled theoretically, depending on the nature of the various processes that act to change them. In particular, we refer to the following processes:

- Attachment, in which a neutral particle and an electron combine, producing a negatively charged ion.
- Diffusion, in which particles diffuse in position space or velocity space. Thermal diffusion is related to particle diffusion, but refers to energy, not particle transport.
- Recombination, in which ions and electrons recombine to form neutral particles; radiation is sometimes emitted.
- Ionization, the inverse of recombination.
- Excitation, in which neutral particles or ions—which are not fully stripped—gain energy, which is evident by orbital electrons moving to higher energy states.
- De-excitation—the inverse of excitation; often, radiation is emitted.

There are many ways in which these processes can occur, such as ionization by electron impact, chemical ionization, or radiation absorption.

It is often surmised that a plasma is electrically neutral, but such a condition usually does not occur when a plasma is in contact with a surface. Under these circumstances, a "sheath" is developed about the surface in which either electrons or ions are the dominant species. Usually, this results in a net electric field in the sheath. Sheaths have considerably different properties than do the neutral plasma, and care must be taken to understand them. The conductivity of a plasma may actually be quite high, often greater than metals.

The composition of the plasma is of paramount importance. Here, one needs to know the mass numbers of all of the ions and neutral particles in the plasma. In many cases, it is desirable to know this as a function of both time and position, and the nature of the diagnostic devices needed to determine this ranges from very simple to very sophisticated indeed.

### 2.2. Plasma Production

Plasmas may be generated by passing an electric current through a gas. Normally, gases are electrical insulators, but there are always a few charge carriers present that can be accelerated by the electric field and can then collide with neutral particles, producing an avalanche breakdown—thus making the plasma. The electric field needed for breakdown can be made with a potential set-up between a pair of electrodes, with an “electrodless” rf (radio-frequency) induction coil, with shock waves, with lasers, or with charged or neutral particle beams. The latter processes can also produce gaseous plasmas if they impinge on a solid target. In addition, heating various materials—usually alkali metals—in ovens or furnaces will cause not only evaporation of neutral particles but also ionization, and plasmas may be made in this way. Many chemical processes can also cause ionization.

## 3. Plasma Physics

### 3.1. Plasma Dynamics

The dynamics of the motion of the charged particles in a plasma are governed by the fundamental equation of motion:

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \qquad (1)$$

where **F** is the force on the charged particle, **E** is the electric field, **B** is the magnetic field, and ***v*** is the charged particle’s velocity.

If one knew all of the values of the electric and magnetic fields, including those produced by all of the particles—self-consistent fields—at the location of each particle, and if collisions between particles could be neglected, then the trajectories of all the particles could be obtained simultaneously with a computer. However, such a computer does not exist, since literally billions of equations would need to be solved simultaneously. In addition, collisions between particles—including charged-particle–neutral-particle collisions—must occur, so such a method cannot be totally practicable. However, much understanding can be gained with numerical simulation of “clumps” or “clouds” of plasmas using modern supercomputers, where upward of a million simultaneous equations can be solved over a reasonable time period.

Thus, we need to develop a means to consider collisional interactions between particles making up the plasmas. Such interactions are classified into two types: elastic and inelastic collisions. In elastic collisions, the kinetic energy, linear momentum, and angular momentum of the two colliding particles are conserved. In inelastic collisions, some of the energy and momentum is changed into or from internal vibration energy and chemical energy (such as chemical bonds), or conducts the processes of ionization, excitation, recombination, or de-excitation, and potentially generates electromagnetic radiation during the process as well.

The most common representation for such interactions is called the collision cross-section. We develop this formulation as follows. Let us assume that a beam of particles of density, $n$ particles cm$^{-3}$; traveling with a velocity, $v$; and of cross-section, A; passes through the plasma a distance, $dx$. Let $N$ be the number of plasma particles/cm$^3$. The number of beam particles colliding with plasma particles per unit time may then be written as:

$$\frac{dn}{dt} = -[(N\sigma Adx)/(Adx)]nv \tag{2}$$

The term, $N\sigma Adx$, is the probability of collision in the volume, $A\ dx$, and $nv$ is the particle current density of incoming beam particles; $\sigma$ is the collision cross-section for this particular process. We may also write $v\ dt = dx$ and $N\ \sigma = p_o p_c$, and we can rewrite Eq. (2) to be:

$$n = n_0 \exp(-p_0 P_{cx}) \tag{3}$$

It is also convenient to write:

$$n = n_0 \exp(p_0 P_c vt) = n_0 \exp(-\nu_c t) \tag{4}$$

introducing an average collision frequency, $\nu_c = \underline{p_o P_c v}$. In the above equations, $P_c$ is the probability of collision for a particular process and $p_o$ is the "reduced" pressure = 273 p/T, which expresses a concentration $N/V$ = 3.54 × 10$^{16}$ $p_o$ molecules/cm$^3$. The term $\underline{p_o P_c}$ has units of 1/length, or $1/(\underline{p_o P_c}) = \lambda$—the mean free path.

Each process has its own cross-section, which in many cases can only be determined experimentally.

-
-
-



**Bibliography**

Blaustein B.C. (ed.) (1969). *Chemical Reactions in Electrical Discharges.* Advances in Chemistry Series No. 80. New York: American Chemical Society. [A compendium of chemical reactions for many different processes.]

Brown S.C. (1959). *Basic Data of Plasma Physics*. New York: Wiley. [The seminal reference to how charged particles interact in actual discharges. It includes cross-section measurements, both as formulas and shown graphically from experiments.]

Bunshah R.F. (ed.) (1992). *Deposition Techniques for Films and Coatings*. Park Ridge, NJ: Noyes. [A practical resource manual for key deposition processes. It is very useful for those who wish to set up their own systems.]

Chen F.F. (1984). *Introduction to Plasma Physics*, *Second Edition*. New York: Plenum. [An excellent introductory text to the subject, written from a physics point of view.]

Coburn J.W. (1980). Plasma chemistry. *Plasma Processes* **2**(2). [A key article that reviews plasma etching.]

Conrad J.R., Dodd R.A., Han S., Madapura M., Scheuer J., Sridharan K., and Worzala F. (1990). *J. Vac. Sci. and Tech.* A p. 1820. [The first paper that describes plasma source ion implantation.]

Holloban J.R. and Bell A.T. (ed.) (1974). *Techniques and Applications of Plasma Chemistry*. New York: Wiley. [A users manual for plasma-chemistry systems.]

Knights J.C. (ed.) (1994). *The Physics of VLSI.* New York: American Institute of Physics. [A review of microelectronic fabrication techniques.]

Lieberman M.A. and Lichtenberg A.J. (1994). *Principles of Plasma Discharges and Materials Processing*, Wiley Interscience: [This text is an approach from both a physics and a chemistry point of view, and is a very good introductory text.]

Mucha J.A and Hess D.W. (1983). *Plasma Etching*. New York: American Chemical Society. [How plasma etching works from a chemistry point of view.]

National Materials Advisory Board. (1985). *Plasma Processing, Report of the National Materials Advisory Board.* Washington, D.C.: National Academy Press. [A plan for development of plasma processing as a technology in a wide range of industries.]

Nowogrozki M. (1984). *Advanced III-V Semiconductor Materials Technology Assessment.* Park Ridge, NJ: Noyes. [Many of these compounds will find use in future plasma treatment systems and this report gives an assessment of their potential.]

Ratner B.D., Chilkoti A., and Lopez G. (1990). Plasma deposition and treatment for biomaterial applications. *Plasma Deposition Treatment and Etching of Polymers* (ed. R. d'Agostino). San Diego, CA: Academic Press. [This is a key report on utilization of plasma technology for biomaterial applications.]

Shohet J.L. (1971). *The Plasma State*. New York: Academic Press. [A basic plasma text written from an electrical engineering point of view.]

Venugapalan M. (ed.) (1971). *Reactions under Plasma Conditions*. New York: Wiley. [Plasma chemistry explained in an understandable way.]

Williams E.F. (1987). Proceedings of Conference on Biomaterials. European Society for Biomaterials, Elsevier [Explains needs and uses for biomaterials.]



## Biographical Sketch

**J. Leon Shohet** received his Ph.D. degree from Carnegie Mellon University, Pittsburgh, PA, USA, in Electrical Engineering in 1961. He served on the faculty of the Johns Hopkins University, Baltimore, MD, USA, before joining the faculty of the University of Wisconsin, USA, in 1966, where he was appointed Professor of Electrical and Computer Engineering in 1971. He has served as the Director of the Torsatron/Stellarator Laboratory, a major Department of Energy fusion research facility, and is the Founding Director of the University of Wisconsin's Center for Plasma-Aided Manufacturing, as well as the Past Chairman of the Department of Electrical and Computer Engineering. Dr. Shohet is a Fellow of the Institute of Electrical and Electronics Engineers (IEEE) and the American Physical Society, and founded the *IEEE Transactions on Plasma Science* in 1973.