CHAPTER 5

The Low Pressure Plasma Processing Environment

5.1 Introduction

A plasma is a gaseous environment that contains enough ions and electrons to be a good electrical conductor. "Plasma processing" is a general term for processes using a plasma environment where the plasma is an essential part of the processing. Often in a PVD processing plasma the degree of ionization is low (i.e. a weakly ionized plasma), such that there are many more gaseous neutrals than there are ions.

Generally in PVD deposition processes, plasmas are used:[1]

- As a source for inert (Ar^+, Kr^+, Hg^+) and/or reactive (O^+, N^+) ions that can be accelerated to high energies.
- As a source of electrons.
- As a means for cleaning surfaces by "ion scrubbing," physical sputtering, or plasma etching.
- For creating new chemical species by plasma chemistry effects such as Si_2H_6 from SiH_4 or O_3 from O_2, etc.
- As a means of "activating" reactive species by forming excited species, radicals, and ions, and adding thermal energy by collision processes.
- As a source of UV radiation.

Plasmas are typically established in low pressure gases though they may be found in atmospheric ambient or higher pressures, where they can be in the form of a corona discharge or an atmospheric arc discharge.

In order to have a good plasma system for PVD processing the system should first be a good vacuum system (Ch. 3). One major difference between a system used for vacuum processing and one used for plasma processing is that often the conductance of the pumping

Handbook of Physical Vapor Deposition (PVD) Processing, ISBN: 9780815520375

system in the plasma system is reduced to minimize the flow of processing gases through the system (Ch. 4). This reduced conductance reduces the ability of the system to pump away system- and process-related contaminants generated during processing. In addition, many contaminants are “activated” in the plasma, making them more chemically reactive. Thus, contamination is often more of a concern in a plasma system than in a vacuum system. Another concern in a plasma system is plasma uniformity, which depends on how the plasma is generated and the geometry of the system, the electrodes, and the fixturing.

If a high dc voltage is applied between two electrodes in a vacuum, the electrical response will depend on the gas pressure. At a very low pressure only the naturally occurring ions, formed by natural radiation, will be collected. As the gas pressure increases, ions and electrons will be accelerated, ions will be generated by electron–atom collisions, and the current will increase. At higher pressures, a normal glow discharge will form a bright spot (cathode spot) on the cathode. Most of the potential drop will occur near the cathode. As the pressure increases further, the cathode spot will maintain the same current density but will grow in size. When the spot covers the cathode, the cathode current density will be a function of the gas pressure and this region is called the abnormal glow discharge region. A plasma will fill the region between the electrodes even though most of the potential drop will be near the cathode, across the cathode fall region, as shown in Figure 5.1. As the pressure increases, the plasma between

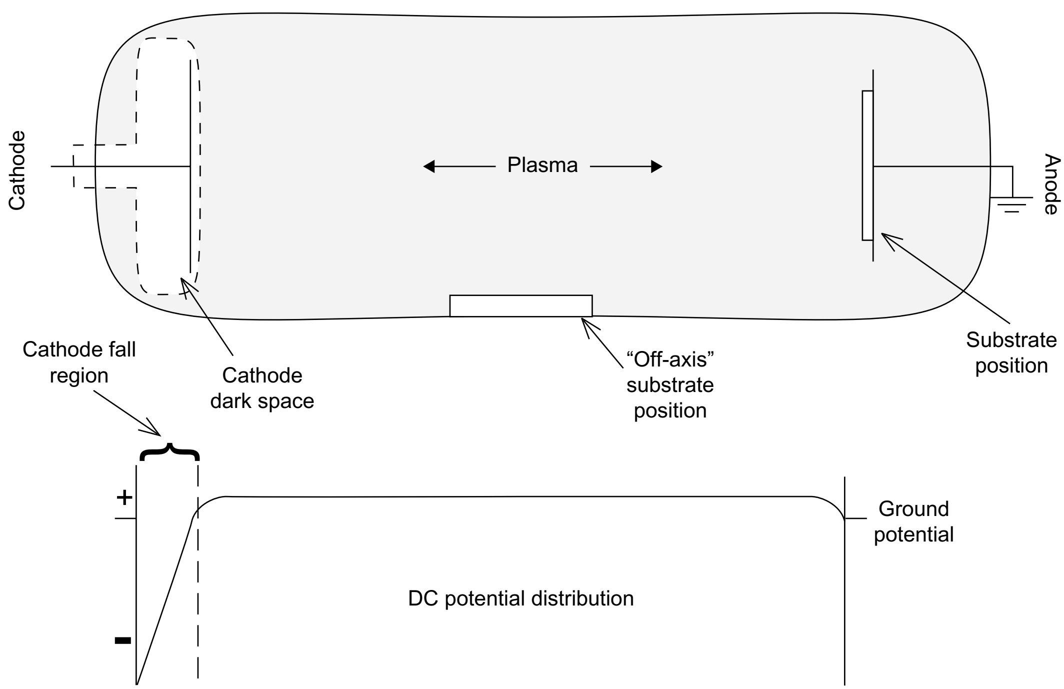


Figure 5.1: Direct Current (dc) Diode Discharge Showing the Potential Distribution Across the Discharge

the electrodes acts as a better and better electrical conductor until finally an arc is formed and the voltage between the electrodes falls and the current density increases.

5.2 The Plasma

A weakly ionized plasma is one that has only a small portion of the gaseous species ionized with the rest being neutrals, some of which may be "excited". An "equilibrium plasma" is one that is volumetrically charge-neutral, having equal numbers of ions and electrons per unit volume. Plasmas are maintained by the continuous introduction of energy, which accelerates electrons to energies that are capable of ionizing atoms by electron–atom collisions. The inelastic collisions between electrons and atoms/molecules in the plasma produce a large number and variety of excited species, radicals, and ions without having to have a high thermal gas temperature, as is necessary in thermal (flame) ionization.

5.2.1 Plasma Chemistry

Plasma is an energetic environment in which a number of chemical processes may occur. Many of these chemical processes occur because of electron–atom collisions.

In a sustained plasma, electrons are accelerated in an electric field. The sources of electrons are:

- Secondary electrons from an ion- or electron-bombarded surface.
- Ionizing collisions in which an atom loses an electron.
- Electrons from a hot thermoelectron-emitting source (hot cathode).
- Electrons from a hollow cathode source.

When heated, some surfaces emit copious amounts of electrons (thermoelectron emission). Tungsten and thoriated tungsten are common examples but lanthanum hexaboride (LaB_6) is an interesting material in that, at a temperature of 1700°C, it has an electron emission of $>20\,A/cm^2$, which is much higher than that of tungsten at the same temperature. Hot surfaces of these materials are used as electron sources in some ion and plasma sources.

Excitation

Excitation is the elevation of outer-shell electrons of the atom to a higher energy state (Sec. 2.3.1). Figure 2.3 shows the energy levels for copper. Excitation may be very short-lived where the electrons return spontaneously to the ground energy state and emit optical radiation, or may be stable where some collision process is necessary to de-excite the atom. These long-lived states are called metastable states. For example, $Ar + e \rightarrow Ar^*$ (metastable) $+ e^-$. Table 5.1 gives the ionization and metastable excitation energies of some atoms.

Table 5.1: Ionization and Metastable Excitation Energies of Various Materials.

First Ionization Energy (eV)			
Ar	15.7	O	13.6
Al	6.0	CH_4	14.1
Au	9.8	C_2H_2	11.6
Cl	12.9	C_6H_6	9.6
Cr	6.7	Cl_2	13.2
F	17.3	F_2	17.8
H	13.5	H_2	15.6
He	24.4	HCl	13.8
Hg	10.3	NO	9.5
Na	5.1	N_2O	12.9
Ne	21.4	O_2	12.5
Second Ionization Energy (eV)			
Ar	27.76	Na	47.0
O	34.93	Cr	16.6
Metastable Energy Levels (eV)			
He	19.82, 20.61		
Ne	16.62, 16.71		
Ar	11.55, 11.72		
Kr	9.91, 9.99		
Xe	8.31, 8.44		

The de-excitation emission spectrum from the plasma is characteristic of the species in the plasma. For example, the emission spectrum (plasma color) of copper is green, that of sodium vapor is yellow, that of mercury vapor is blue–green, that of argon is violet, that of oxygen is yellow–white, that of nitrogen is red–yellow, and that of air is reddish–pink. The emission spectrum may be used for plasma diagnostics and to monitor and control the density of species in the plasma.

Ionization by Electrons

Positive ions are formed by atoms or molecules suffering an inelastic collision with an energetic electron in which an electron is lost from the atom or molecule (electron impact ionization). The degree of ionization of the plasma depends strongly on the electron density and energy distribution in the gas.

$$Ar + e^- \rightarrow Ar^+ + 2e^-$$
$$O_2 + e^- \rightarrow O_2^+ + 2e^-$$

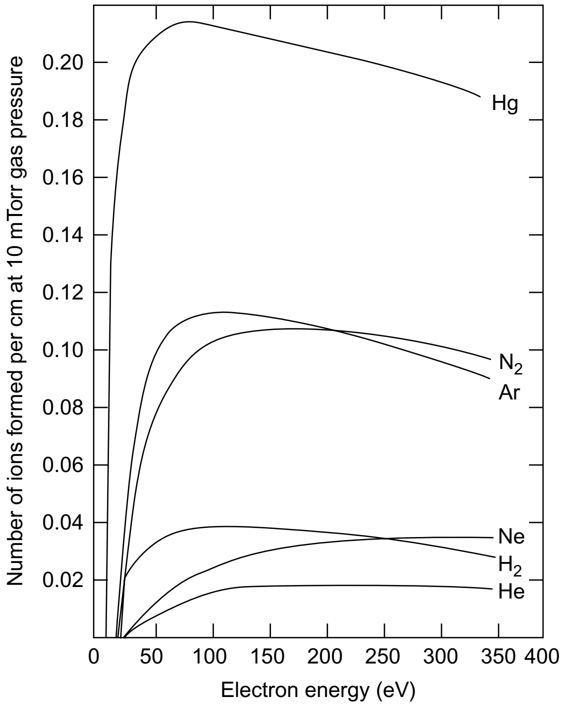


Figure 5.2: Relative Ionizability of Various Gases (and Vapors – Hg)

The maximum ionization probability (cross-section) occurs when the electrons have an energy of about 100 eV. At high electron energies, the cross-section for collision is low and high energy electrons can move through the gas rather easily. Figure 5.2 shows the relative ionizability of various gases (and vapors – Hg). Note that the optimum energy for ionization is about 100 eV electrons for all the gases.

The energy necessary to remove the first electron, the second electron, etc. is characteristic of the specific atoms. Table 5.1 gives the first and second ionization potentials for various atoms.

In electron attachment ionization, negative ions are formed by electron attachment in the gas. These plasmas can be very electronegative and are used in processes such as plasma anodization.

$$O_2 + e^- \rightarrow O^-_2$$

Dissociation

Dissociation is the electron impact fragmentation of molecules to form charged (radicals) or uncharged fragments of the molecule.

$$O_2 + e^- \rightarrow 2O^\circ + e^-$$
$$O_2 + e^- \rightarrow O^\circ + O^-$$
$$SF_6 + e^- \rightarrow SF^-{}_5 + F^\circ$$
$$H_2O + e^- \rightarrow H^\circ + OH^-$$

Penning Ionization and Excitation

Penning ionization and Penning excitation is the ionization (or excitation) of an atom by the transfer of the excitation energy from a metastable atom whose excitation energy is greater than the ionization (or excitation) energy of the other atom. The cross-section for Penning ionization is greater than that for electron impact ionization so Penning ionization is an important ionization mechanism in "mixed plasmas" containing more than one species. For example, a copper atom moving through an argon plasma can be ionized by collision with metastable argon atoms.

$$Ar^* \text{ (metastable)} + Cu \rightarrow Ar + Cu^+ + e^-$$

Argon has metastable states of 11.55 and 11.75 eV and the ionization energy of copper is 7.86 eV. Thus, a copper atom colliding with a metastable argon atom is easily ionized. Metastable atoms may be very effective in ionizing other species by collision. For example, a small amount of nitrogen in a neon plasma greatly facilitates the maintenance of the neon discharge.

Charge Exchange

Charge exchange occurs when an energetic ion passes close to a thermal neutral and there is a transfer of an electron forming an energetic neutral and a thermal ion. This process gives rise to a spectrum of energies of the ions and neutrals in a plasma.

Photoionization and Excitation

In photoionization or photoexcitation processes, photon radiation is absorbed by a molecule to the extent that ionization or excitation occurs. This process is important in "laser-induced" chemical processing.

$$O_2 + hv \rightarrow O + O^+ + e^-$$

where hv is the energy of a photon

An example of this process is laser-induced CVD, where the radiation frequency is tuned to the vibrational frequency of the precursor molecule, to enhance decomposition. This resonance absorption/excitation is the basis of laser-induced fluorescence, which may be used to determine species on a surface or in the gas phase.

Electron–Ion Recombination

Electron–ion recombination (neutralization) occurs when ions and electrons combine to form a neutral species.

$$Ar^{+} + e^{-} \rightarrow \text{surface} \rightarrow Ar^{\circ}$$

The electron–ion recombination process occurs mostly on surfaces and releases the energy taken up in the ionization process. This recombination, and the associated energy release, aids in desorption in the ion scrubbing of surfaces (Sec. 13.11.1).

Plasma Polymerization

In plasma polymerization, monomer vapors are crosslinked to form a polymer either in the plasma or on a surface in contact with the plasma. The process can occur with either organic or inorganic monomers. Examples are the formation of amorphous silicon (a-Si : H) from SiH_4 and hydrocarbon polymer films from gaseous hydrocarbon species.

Unique Species

Species in the plasma can combine to give unique species that can have special properties such as high adsorption probabilities.

$$2SiH_4 \rightarrow \text{plasma} \rightarrow Si_2H_6 + H_2$$
$$O_2 \rightarrow \text{plasma} \rightarrow O^{\circ} + O_2 \rightarrow O_3$$

Plasma "Activation"

Many of these plasma processes serve to plasma activate gases; i.e., to make them more chemically active by dissociation, fragmentation, ionization, excitation, forming new species, etc. These activated gases impinge on the substrate surface or, if ionized, can be accelerated to the substrate by a substrate bias, thereby enhancing "reactive deposition" and "reactive etching" processes. Generally, contaminant gases and vapors, such as water vapor and O_2, in plasma-based processes are more significant than the same contaminant level in a vacuum-based deposition process because of plasma activation.

Cross-sections and Threshold Energies

Many plasma processes are characterized by cross-sections for processes and threshold energies for chemical processes. The cross-sections for interactions are often far greater than the physical dimensions. For example, the cross-section for $O_2 + e^- \rightarrow O_2^+ + 2e^-$ is $2.7 \times 10^{-16}\,cm^2$. Both the cross-section and the threshold energy are important for reaction. For example, SF_6 and CF_3Cl have a high cross-section and low threshold energy (2–3 eV) for electron-dissociative attachment. Thus, they act as electron scavengers in a plasma. CF_4 has a low cross-section and high threshold energy (5–6 eV) for electron-dissociative attachment, and CCl_4 is not activated by electron attachment at all. SF_6 and CF_3Cl are much more easily activated than is CCl_4 or CF_4.

Thermalization

Energetic atoms, ions, or molecules moving through a gas lose energy by collisions with the ambient gas molecules, scatter from their original direction, and become thermalized. Figure 5.3 shows the distance for thermalization for atoms of various masses and energies in various pressures of argon gas.

5.2.2 Plasma Properties and Regions

Plasma properties include: total particle density, ion and electron densities, ion and electron temperatures, the density of various excited species, and gas temperature. If there is a mixture of gases, the partial densities and flow rates of the gases can be important. In a plasma these properties can vary from place to place. In general, a low pressure plasma will not sustain a pressure differential except in the region of a pumping or gas-injection port. However, local gas temperature variations can create variations in the atom/molecular/ion densities, particularly in the vicinity of a cathodic surface. This density variation can be reflected in the deposited film properties due to differing bombarding fluxes and differing concentrations of activated reactive species. This can produce problems with position equivalency. In some regions there can be a different number of electrons and ions in a given volume and a space charge region is established.

Typical property ranges for weakly ionized plasmas at low pressure (10^{-3} Torr) are:

Ratio of neutrals to ions	10^7–10^4 : 1
Electron density	10^8–$10^9\,cm^3$
Average electron energy	1 to 10 eV
Average neutral or ion energy	0.025 to 0.035 eV (higher for lower pressures)

For weakly ionized plasmas of molecular species, the radical species can outnumber the ions but are still fewer than the number of neutrals.

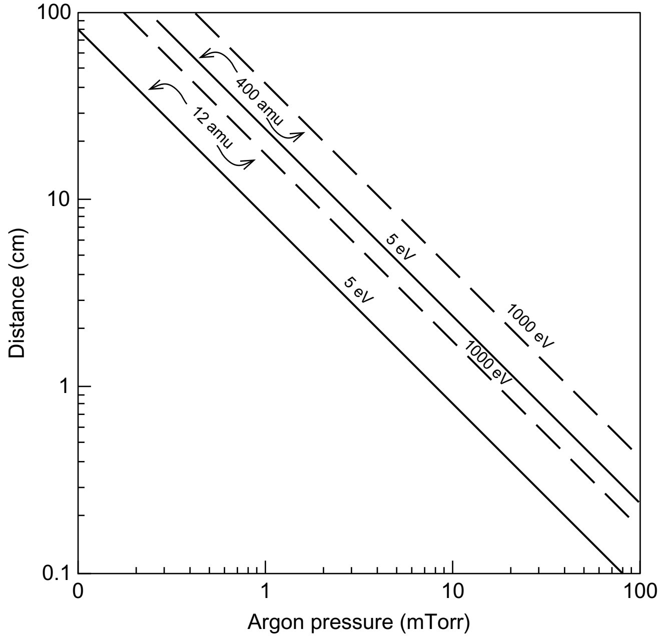


Figure 5.3: Thermalization

Strongly ionized plasmas are ones where a high percentage of the gaseous species is ionized. In microwave plasmas and arc plasmas, the ionization can almost be complete. One advantage of the microwave plasma is that, even though the ionization is high, the particle temperatures are low.

High enthalpy plasmas are those that have a high energy content per unit volume, and they are sometimes called thermal plasmas. Thermal plasmas have a high particle density, are strongly ionized, and are of gases that have high ionization energies. This type of plasma is used in plasma spray processes.

In plasma discharges it has been shown that the gas flow is affected by the electric fields and associated ion motion (discharge pumping).[2,3] This gas flow can entrain molecules injected into the plasma region and give preferential mass flow. Plasmas may be easily steered by moving the electrons in a weak magnetic field with the ions following the electrons in order to retain volumetric charge neutrality.

Plasma-generation Region

In the plasma-generation region, electrons and ions are accelerated in an electric field. At low pressures, these particles can attain high kinetic energies and may damage surfaces placed in that region.

Afterglow or "Downstream" Plasma Region

As one moves away from the plasma-generation region, the plasma temperature decreases, ions and electrons are lost due to recombination, and the number of energetic electrons is diminished. This region is called the plasma afterglow region, and in deposition and etching processes this position is called the "remote" or "downstream" location.[4] Other gas or vapor species can be introduced into this region to "activate" them by collision with the metastable species in the plasma. Substrates placed in this location are not exposed to the energetic electron bombardment conditions found in the plasma-generation region.

The "Disappearing Anode Effect"

Non-rf plasmas require an anode and a cathode. In sputtering, the cathode is eroded by ion bombardment. In reactive sputter deposition the sputtered materials react with a gas in the ambient or with a co-deposited material to form a compound on the substrate. If the compound that is formed is electrically insulating, a portion of the material not on a substrate may cover a part of the anode. Over a period of time this will change the configuration of the plasma and the plasma properties. The covering of the anode is called the "disappearing anode effect" in reactive sputter deposition of dielectric materials.

Measuring Plasma Parameters

There are many techniques used to characterize plasmas.[5] Analysis of the optical emission from de-excitation is probably the most common technique used to analyze and control plasmas.[6] For example, OES is used to monitor the plasma etching process by monitoring the presence of the reactive species that are consumed or, more often, the reactant species formed by the reactions. The magnitude and shape, as a function of time of the emission curve, can give an indication of the etch rate and the etching uniformity. The completion of the etching process is detected by the decrease of the emission of the reactant species (endpoint analysis). Actinometry compares the emission interactions of the excited states of reference and subject species to obtain the relative concentrations of the ground states. Doppler broadening of the emission lines can be used to indicate plasma temperature. Optical emission characteristics are used both for process monitoring and for process control.

Laser-induced fluorescence spectroscopy is used to investigate plasma–surface interactions and for impurity diagnostics in plasmas. Optical absorption spectroscopy can also be used to characterize the gaseous and vapor species and temperature in a gas discharge.

Large-area electrodes determine the plasma potential in the nearby volume. Small-area probes, such as Langmuir probes, do not significantly affect the plasma, and the electron and ion densities in a plasma can be measured using these probes. A small insertable/retractable probe that profiles the plasma along its track is commercially available.

The electron density in the path of a microwave adsorbs energy and attenuates the transmitted signal. This microwave attenuation can be used to analyze the plasma density. A plasma has an effective index of refraction for microwave radiation. By measuring the phase shift of transmitted/received microwave radiation as it passes through the plasma, the charge density can be determined. Generally the phase shift is determined by interferometric techniques.

5.3 Plasma–surface Interactions

Electrons and ions are lost from the plasma to surfaces – there is relatively little recombination in the plasma volume. Under equilibrium conditions, an equal number of ionized molecules are generated as are lost from the plasma. When surfaces, electrodes, or electric fields are present, the plasma may not be volumetrically neutral in their vicinity.

5.3.1 Sheath Potentials and Self-bias

The plasma sheath is the volume near a surface which is affected by loss of plasma species to the surface. Electrons have a higher mobility than ions so electrons are lost to the surface at a higher rate than are ions; this produces a potential (sheath potential) between the surface and the plasma. If the surface is grounded, the plasma is positive with respect to ground. If the surface is electrically floating and the plasma is in contact with a large-area grounded surface, the floating surface will be negative with respect to ground. The sheath potential is dependent on the electron energy, the electron flux, and the area of the surface. The sheath potential can vary from a few volts in a weakly ionized dc diode discharge to 50–75 volts when energetic electrons impinge on the surface at a high rate. The sheath potential is the negative self-bias that accelerates positive ions from the plasma to the surface, producing "ion scrubbing" of the surface at low potentials and physical sputtering of the surface at higher potentials (Sec. 13.11). This physical sputtering can be a source of contamination from surfaces in a plasma system.

It is possible for a surface in contact with a plasma to generate a positive self-bias. This occurs when electrons are kept from the surface by a magnetic field but positive ions reach the surface by diffusion. An example is in the post cathode magnetron sputtering configuration with a floating substrate fixture, which can attain a positive self-bias.

5.3.2 Applied Bias Potentials

Because the electrons have a very high mobility compared to positive ions, it is impossible to generate a high positive bias on a surface in contact with a plasma. The negative potential between the plasma and a surface can be increased by applying an externally generated negative potential to the surface. This applied potential can be in the form of a continuous dc, pulsed dc, alternating current (ac), or rf potential. This applied bias can accelerate positive ions to the surface with very high energies.

5.3.3 Particle Bombardment Effects

Energetic ion bombardment of a surface causes the emission of secondary electrons. Metals generally have a secondary electron emission coefficient of less than 0.1 under ion bombardment while the secondary electron emission coefficients of oxide surfaces are higher. Secondary electron emission from electron bombardment is much higher than from ion bombardment.

Energetic ion bombardment of a surface can cause physical sputtering of surface material (Sec. 7.2). If the bombarding species are chemically reactive they can form a compound layer on the surface if the reaction products are not volatile. If this surface layer is electrically insulating or has different electrical properties than surrounding surfaces, surface charges can be generated that cause arcing over the surface. If the reaction products are volatile then plasma etching of the surface occurs.

5.3.4 Gas Diffusion into Surfaces

The adsorption of gaseous species on a surface exposed to a plasma is poorly understood but one would expect that adsorption in a plasma would be greater than in the case of gases, due to the presence of radicals, unique species, image forces, surface charge states on insulators, and other such factors. This may be an important factor in reactive deposition processes.[7]

Absorption of a gas into the bulk of the material involves adsorption, possibly molecular dissociation, then diffusion into the material. The process of injecting gas into a surface is called "charging". Diffusion of gases, particularly hydrogen, into metals can be enhanced by exposure to a hydrogen plasma and low energy ion bombardment. Reasons for the rapid absorption of hydrogen into surfaces include:

- There is no need for molecular dissociation at the surface.
- Surface cleaning by the hydrogen plasma.
- Implantation of accelerated hydrogen ions into the surface, producing a high chemical concentration and thus increasing the "chemical potential," which is the driving force for diffusion.

5.4 Configurations for Generating Plasmas

In generating and sustaining plasmas, energy is imparted to electrons by an electric field and the energetic electrons create ionization by electron–atom impact.

5.4.1 Electron Sources

Electrons in a plasma originate from: (1) secondary electrons from an ion or electron-bombarded surfaces (secondary electron emission), (2) ionizing collisions, (3) electrons from a thermoelectron-emitting source (hot cathode), and (4) presence of a hollow cathode configuration (e.g. hole in a cathodic surface).

5.4.2 Electric and Magnetic Field Effects

Electric fields are formed around solid surfaces that have a potential on them. The locations in space that have the same potential with respect to the surface are called equipotential surfaces. When the surface is flat or nearly so, the equipotential surfaces will be conformal with the solid surface. When the solid surface has a complex morphology, the equipotential surfaces will not be able to conform to the solid surface configuration and will "smooth out" the irregularities. Surfaces with closely spaced features, such as an open mesh (high transmission) grid, appear as a solid surface to the electric field. The separation between the equipotential surfaces establishes the electric field gradient. Electrons and ions are accelerated normal to the equipotential surfaces. Figure 5.4 shows some equipotential surfaces and the effects of curvature on the equipotential surfaces. The variation of field over a non-smooth surface leads to variations in the bombardment of the surfaces by ions.

Magnetic fields in space can be generated in a number of ways, including:

- Internal fixed permanent magnets
- External electromagnets
- Internal moving permanent magnets
- External permanent magnets

When using permanent magnets, care must be taken to ensure that the magnetic field strength does not degrade with time. This is particularly a problem if the magnets are heated. The magnetic field distribution in space can be measured using Hall-effect probes. Figure 5.5 shows some magnetic field configurations.

Electrons, and to a lesser extent ions, will be affected by the magnetic field and magnetic field strength. If the electron path is parallel to the magnetic field lines, the electron will not be affected by the magnetic field. However, if there is any component of the electron trajectory that is normal to the magnetic field line, the electron will spiral around the field lines. If the electron trajectory is normal to the magnetic field the electron will be trapped in a closed path. The higher the magnetic field strength, the more rapid the circulation and the smaller the diameter of the orbit. This is the basis for the high frequency Klystron tubes developed during World War II.[8]

Low strength (50–500 gauss) magnetic fields affect the motion of electrons but not ions. In a vacuum, an electron with a velocity vector perpendicular to the magnetic field vector is

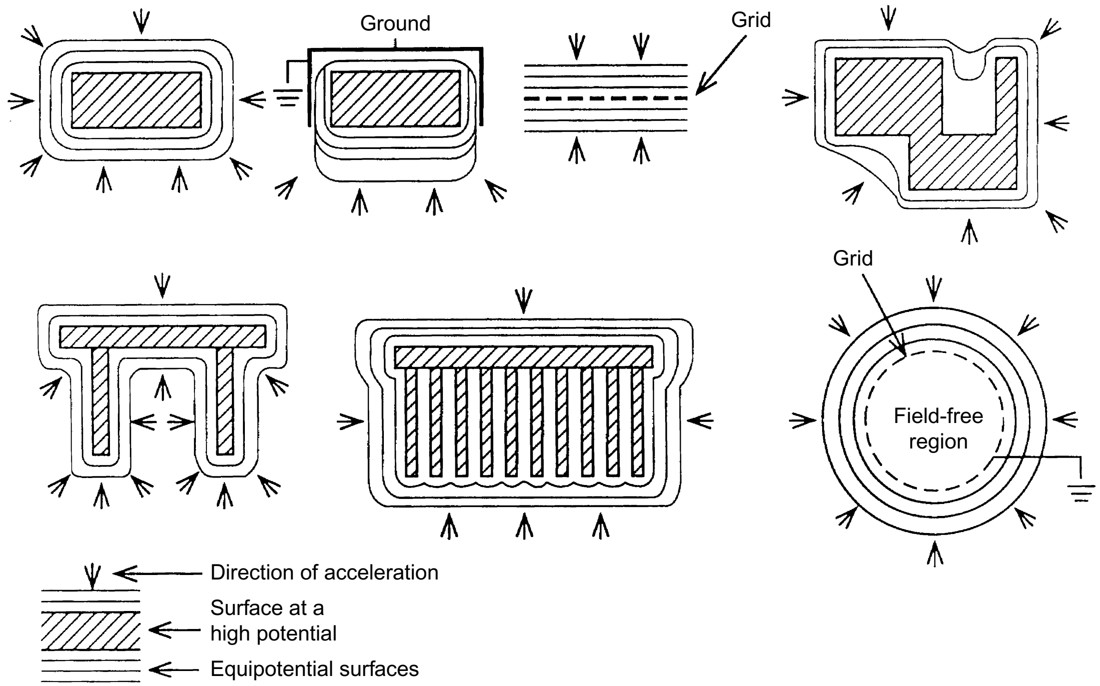


Figure 5.4: Equipotential Surfaces and Ion Bombardment Around Various Solid Surfaces

confined to a circular path around the magnetic field lines with radius, r, (gyro radius) and frequency, φ, (gyro frequency) given by

$$r = Mv_p/e\mathbf{B}, \varphi = e\mathbf{B}/M \tag{5.1}$$

where
M = mass
v_p = velocity perpendicular to magnetic field
$\mathbf{B}$ = magnetic field strength
e = charge

If there is both an electric, **E**, and magnetic, **B**, field present, the electrons have a drift velocity perpendicular to the $\mathbf{E} \times \mathbf{B}$ plane in addition to spiraling around the magnetic field lines. If there is a gas present, collisions cause the electrons to be scattered from their spiral path. After scattering, the electrons begin a new spiral path. They will tend to be trapped where the **E** and **B** fields are normal to each other and this will be the region of maximum ionization. The positive ions will be accelerated to the cathode surface by the electric field.

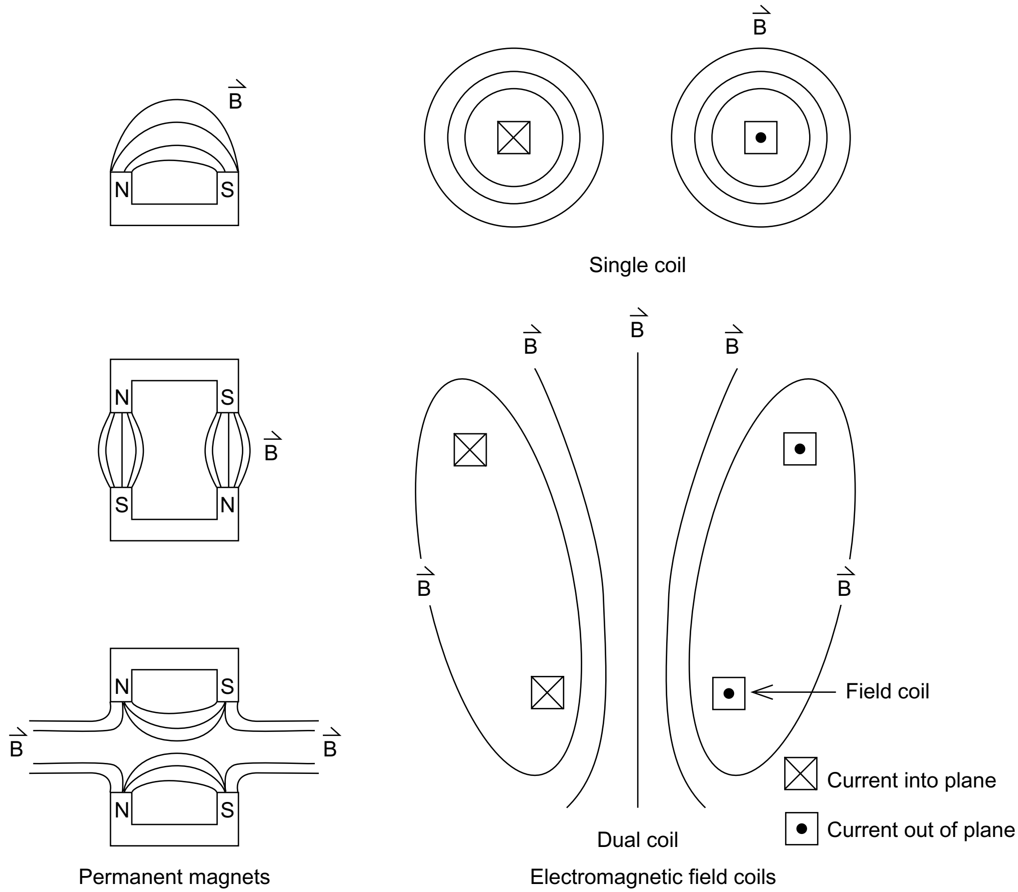


Figure 5.5: Magnetic Field Configurations

5.4.3 Direct Current (dc) Plasma Discharges

The cold cathode dc diode discharge operates in the abnormal glow discharge region where the cathode current density depends on the applied voltage. Figure 5.1 shows a dc diode discharge configuration and the potential drop across the interelectrode space. The cathode fall region is where most of the potential drop in a dc discharge is to be found.

Substrates may be positioned either at a position on the anode (ground) or at an "off-axis position" to avoid bombardment by secondary electrons accelerated away from the cathode.

In the dc diode discharge the cathode (negative) potential attracts ions from near the edge of the plasma region and they are accelerated across the cathode fall region to impinge on the cathode. The impinging ions and energetic neutrals, produced by charge exchange collisions, cause the ejection of secondary electrons which are then accelerated back across the cathode fall region and create ions which sustain the discharge. Thus, under equilibrium conditions, enough electrons are produced to create enough ions to create enough electrons to sustain the discharge. If conditions such as potential, gas species, or gas pressure change, the equilibrium conditions will change. The energetic ion bombardment of the cathode surface also results in physical sputtering.

The ions being accelerated to the cathode will experience physical collisions in the gas phase and lose some of their energy. Some of the ions being accelerated to the cathode may become neutralized by charge exchange processes and this produces a spectrum of energetic neutral species. The result is a spectrum of energetic ions and neutrals bombarding the cathode with few of the ions reaching the surface with the full cathode fall potential. The energetic neutrals formed are not affected by the electric field and may bombard non-electrode surfaces near the target, causing sputtering and film contamination. The dc diode (non-pulsed) configuration requires that the cathode be of an electrically conductive material since a dielectric cathodic surface will build up a positive surface charge that will prevent further high energy ion bombardment.

The electrical current measured in the dc diode circuit is the sum of the ion flux to the target and the secondary electron flux away from the surface. Therefore, the cathode current density and applied cathode voltage do not specify the flux and energy of the impinging ion current! However, these measurements (along with gas pressure) are typically used to establish and control the plasma conditions. Often, the discharge specification is in watts per cm^2 of the cathode surface. Most of the bombardment energy goes into cathode heating, requiring active cooling of the cathode in most cases.

When the dc discharge is first ignited at a constant pressure and voltage, there is a decrease in cathode current with time.[9] This is due to removing the oxides, which have a high secondary electron emission coefficient, from the cathode surface, and heating of the gas, which reduces its atomic/molecular density. The plasma is not in equilibrium until the discharge current becomes constant.

In the dc diode configuration the secondary electrons that are accelerated away from the cathode can reach high energies and impinge on the anode or other surface in the system. This can give rise to extensive heating of surfaces in the dc diode system. In the dc diode discharge configuration, the plasma-generation region is primarily near the cathode; however, the plasma fills the contained volume. This plasma can be used as a source of ions for bombardment, or for activation of reactive species.

In order to sustain a discharge, the secondary electrons must create enough ions to sustain the discharge. If the anode or ground surface is brought too close to the cathode, the discharge is extinguished. This effect can be used to confine the dc discharge to areas of the cathode surface where bombardment is desired by using a ground shield in close proximity to surfaces where bombardment is not desired. For example, in argon at about 10 mTorr pressure, the minimum separation is about 0.5 centimeters. If a ground shield is closer than this to the cathode, the discharge is extinguished between the surfaces.

Shields near the high voltage electrode cause curvature of the equipotential lines in the vicinity of the shields, as shown in Figure 5.4. This field curvature can result in focusing or diverging of the electron or ion trajectories, since charged species are accelerated in directions normal to the field lines. This focusing can affect the heating and sputter erosion pattern on the cathode surface.

In a hot cathode dc diode discharge, hot thermoelectron-emitting surfaces at a negative potential emit electrons that provide the electrons to sustain the discharge. The hot cathode discharge can be operated at a lower pressure than the cold cathode dc discharge since the electron flux does not depend on the ion flux. Very high plasma densities can be achieved in a hot cathode system.

In the triode configuration, the plasma is established between a cathode and anode and ions are extracted from the plasma by a third electrode using a dc or rf potential to give bombardment of a surface. The triode configuration suffers from a non-uniform plasma density along its axis, particularly if high currents of ions are being extracted – this results in non-uniform bombardment of a biased surface. Often the triode system uses a hot cathode and the electrons are confined by a weak magnetic field (50–500 gauss) directed along the anode–cathode axis.

The dc diode discharge cannot be used to sputter dielectric target materials, since charge buildup on the cathode surface will prevent bombardment of the surface. If there are reactive gases in the plasma their reaction with the target surface can lead to the formation of a surface that has a different chemical composition from the original surface. This change in composition leads to "poisoning" of the cathode surface and thus changes the plasma parameters. In the extreme, poisoning will cause bombardment of the cathode to cease due to surface charge buildup. If an insulating surface forms on the dc cathode, charge buildup will cause arcing over the surface.

The suppression of arcs generated in the dc discharge (arc suppression) is important to obtaining stable performance of the dc power supply, particularly when reactively sputter depositing dielectric films. Arcing can occur any time a hot (thermoelectron-emitting) spot is formed or when surface charging is different over surfaces in contact with the plasma. Arc suppression is obtained by momentarily turning off the power supply or by applying a positive voltage pulse when an arc is detected.

Balanced Magnetrons

In surface magnetron plasma configurations, the electric (**E**) (vector) and magnetic (**B**) (vector) fields are used to confine the electron path to be near the cathode (electron-emitting) surface. An electron moving with a component of velocity normal to the magnetic field will spiral around the magnetic field lines and its direction will be confined by the magnetic field. The frequency of the spiraling motion and the radius of the spiral will depend on the magnetic field strength. The interaction of an electron with the electric and magnetic fields depends on the magnitude and vector orientation of the fields ($\mathbf{E} \times \mathbf{B}$). For example, if the magnetic field is parallel to a surface and the electric field is normal to the surface, an electron leaving the surface will be accelerated away from it and will spiral around the magnetic field. There will also be a resulting motion of the electron normal to the $\mathbf{E} \times \mathbf{B}$ plane ($\mathbf{E} \times \mathbf{B}$ drift). If the magnetic field is shaped in such a way as to allow a closed path for these electrons moving normal to the magnetic field then a "circulating current" is established above the surface. This circulating current may be several times the current measured in the external electrical circuit. The plasma thus formed is confined near the cathode surface.

In magnetron discharge configurations, the surface may be planar, a post or cylinder, a cone, or any surface of revolution. Figure 5.6 shows a planar magnetron configuration for confining electrons near a surface. Electron–atom collisions (and ionization) in a gas environment form a plasma near the surface. Using a magnetron configuration, plasmas can be sustained at a few tenths of an mTorr in argon. The magnetron is typically driven with a continuous dc or a pulsed potential (unipolar or bipolar).

Magnetic fields can be generated using permanent magnets or electromagnets (Sec. 5.4.2). Permanent magnets have the advantage that they may be placed so as to position the field lines in a desirable manner; this is harder to do with electromagnets in some configurations. Electromagnets may be used in a two-coil Helmholtz arrangement to produce a space with nearly parallel magnetic field lines. Magnetic pole pieces may also be used to give nearly parallel magnetic field lines. Magnetic fields pass easily through non-magnetic materials, such as aluminum, but magnetic materials must be "saturated" before the magnetic field can penetrate through them.

A major problem in using magnetic fields is the difficulty in obtaining a uniform field over a surface. This non-uniformity in the magnetic field produces a non-uniform plasma. This plasma non-uniformity means non-uniform bombardment of the cathode surface and non-uniform sputtering of the cathode material. In order to increase uniformity the plasma can

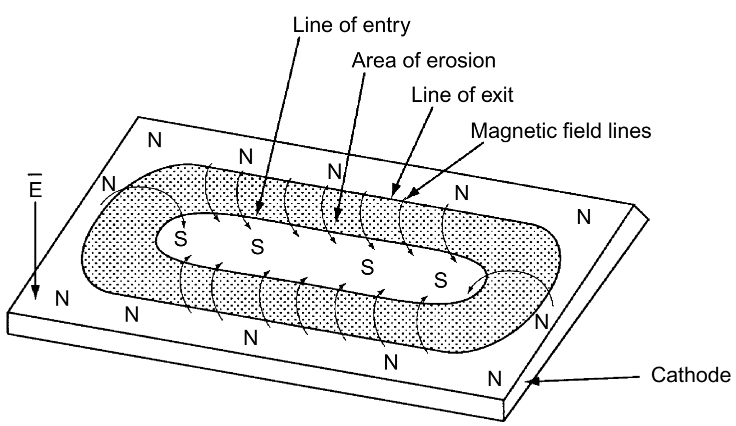


Figure 5.6: Planar Magnetron

be moved over the target surface by moving the magnetic field or the target surface may be moved in the magnetic field.

An rf bias can be superimposed on the continuous dc potential in order to establish a plasma away from the cathode. This is useful in ion plating and reactive sputter deposition where the plasma is used to activate the reactive species and provide ions for concurrent ion bombardment of the growing film. When an rf bias is used with a dc power supply, there should be an rf choke in the dc line to prevent rf from entering the dc power supply.

Unbalanced Magnetrons

"Unbalanced magnetron" is the term given to magnetic configurations where some of the electrons are allowed to escape. Most magnetrons have some degree of "unbalance" but, in the application of unbalanced magnetrons, the magnetic fields are deliberately arranged to allow electrons to escape. These electrons then create a plasma away from the magnetron surface. This plasma can then provide the ions for bombardment of the substrate during ion plating and/or can activate a reactive gas in reactive deposition processes. The magnetic field for unbalancing the magnetron configuration can be supplied either by permanent magnets or by electromagnets. Some unbalanced magnetron configurations are shown in Figure 5.7.

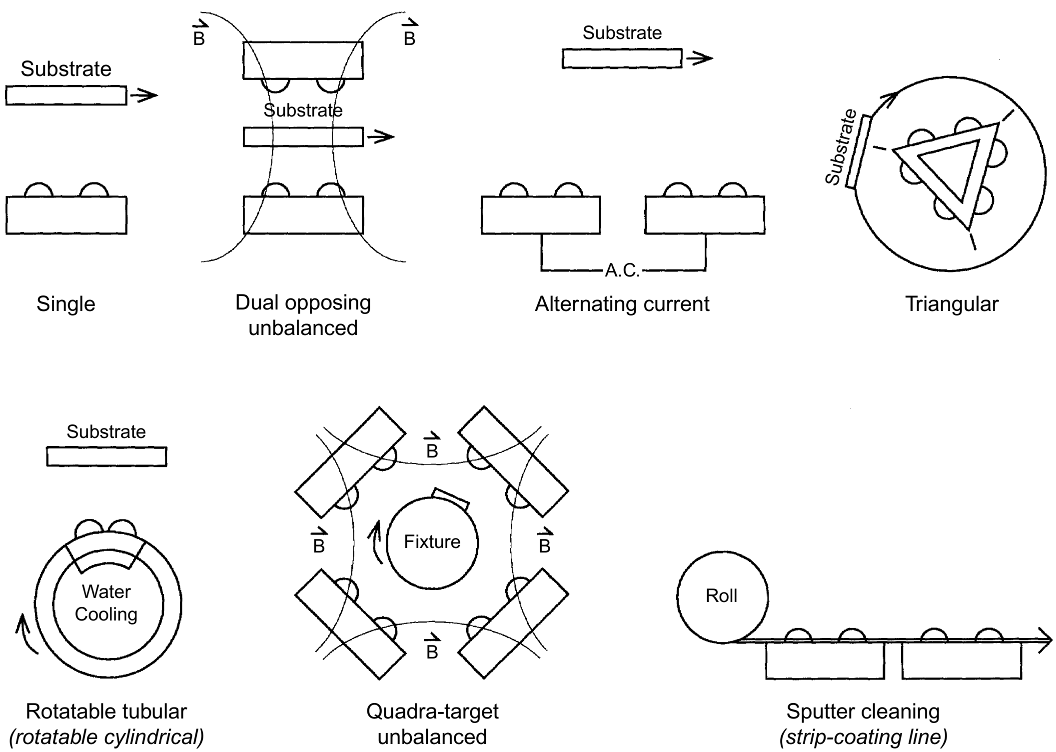


Figure 5.7: Some Single Magnetron and Multiple Magnetron Configurations

Unbalanced magnetrons are often used in a dual arrangement where the escaping field of the north pole of one magnetron is opposite the south pole of the other magnetron. This aids in trapping the escaping electrons. The use of four magnetrons, as shown in Figure 5.7, is called a closed (or linked) field configuration.

5.4.4 Pulsed Power Plasmas

Plasma discharges may also be formed by pulses of voltage (power). Figure 5.8 shows some of the waveforms that may be used. The percentage of time that the processing power (negative potential on a target or substrate) is above zero is called the duty cycle. The off time is the percentage of time in which the voltage is zero or positive. Pulsed power may be in the form of pulsed dc, low frequency (50–60 Hz) ac, mid-frequency (25 to 250 kHz) ac, or high frequency ac (e.g. 13.56 MHz rf)[a]. The power delivered to an electrode is generally the

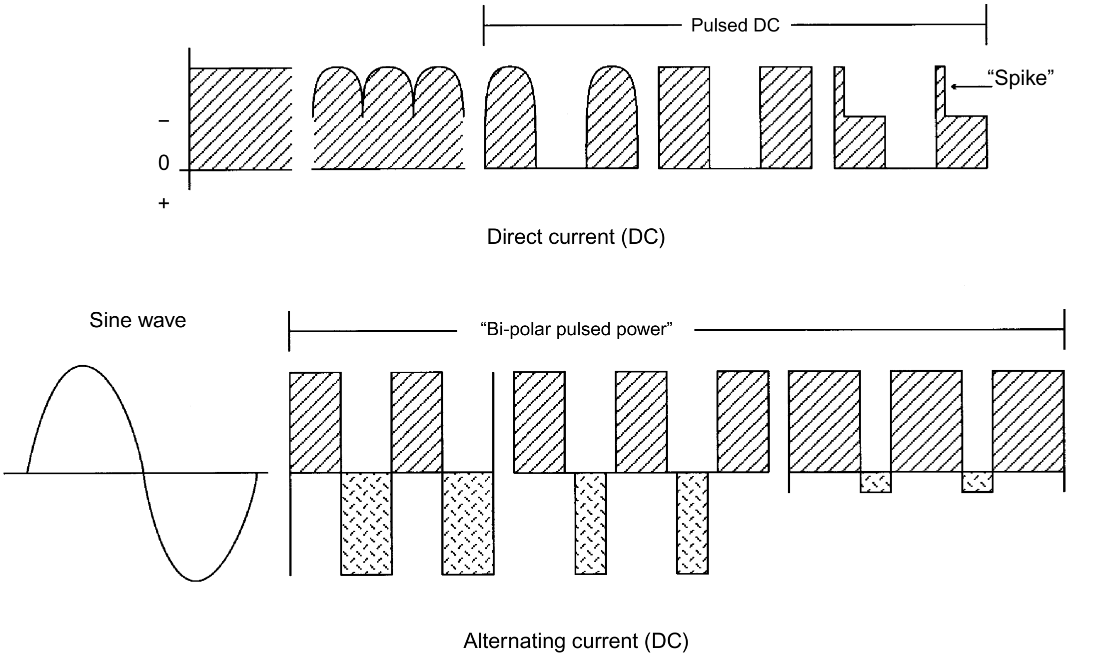


Figure 5.8: Voltage Waveforms

[a] The most common definition of direct current (dc) is that the electrons flow only in one direction in a circuit, while in alternating current (ac) the direction of flow of electrons (current) in the circuit periodically reverses direction. This gets somewhat confused in some power supplies where there are negative pulses and positive pulses generated by separate circuits (Figure 5.8). This is sometimes called bipolar dc, which, I think, is an oxymoron. I will refer to such waveforms as bipolar power. The discussion may be confused even further by the fact that if you suddenly turn off a negative dc voltage (e.g. Figure 5.8), the inductance in the circuit will cause a positive pulse before the voltage goes to zero. Again, I think this has to be called a bipolar pulse since the electron flow reverses direction. So, to have a pure pulsed negative dc you would have to block the positive reverse current.

average of the power over a cycle (e.g. at 50% duty cycle a 4 $W_{(peak)}/cm^2$ will appear as 2 W/cm^2 on a power meter).

If the pulse frequency (either dc or ac) on an electrode is less than several kHz, the plasma will extinguish and reignite on every cycle because the electrons and ions will be lost to the various surfaces. If a dual electrode is used, the cathodic electrode may be alternated between electrodes and the plasma will be continuous (e.g. the common neon sign). If the pulse frequency is above ~25 kHz the plasma will not be completely extinguished (an "afterglow" will remain) and the discharge will not have to reignite from an ion-free condition.

In pulsed PVD processing, dc unipolar waveforms of Figure 5.8d,e are used and the voltage rise and fall is very rapid during the pulse. In bipolar pulsed PVD, the voltage polarity alternates between negative and positive, perhaps with an off time. The bipolar pulse can be symmetric, where the positive and negative pulse heights are equal and the pulse duration can be varied or asymmetric with the relative voltages being variable as well as the duration time. Figure 5.8 show some bipolar waveforms. Generally, in asymmetric bipolar pulse magnetron sputter deposition (for example), the negative pulse (e.g. −400 V) is greater than the positive pulse (e.g. +100 V) and the negative pulse time is 80–90% of the voltage cycle and the positive pulse is 20–10% of the voltage cycle.

In bipolar pulse sputtering, during the positive bias (and off time), electrons can move to the surface from the plasma and neutralize any charge buildup generated during the negative portion of the cycle. During the negative portion of the cycle, energetic ion bombardment can sputter the surfaces.

Pulsed dc power can be obtained by switching a continuous dc or sine wave power supply with auxiliary electronics, or from a specially designed pulsed power supply that generally allows more flexibility as to waveform. The pulsed power supply generally incorporates arc suppression that operates by turning off the voltage or by applying a positive voltage when the arc initiates.

In pulsed power discharges, the discharge is ignited at certain points and spreads over the surface.[9] The ignition is a function of the gas/vapors present as well as the geometry of the cathode.

HIPIMS/HPPMS/HIPPMS and MPP/HIPIMS+

A special and very important type of pulse voltage waveform (patented by V. Kouznetsov) is used in high power pulsed magnetron sputtering (HPPMS), otherwise called high power pulse magnetron sputtering (HIPPMS) or high power impulse magnetron sputtering (HIPIMS[b] or HIPIMS).[10] In this waveform, high peak voltages (500–3000 volts) and very high peak

[b] At present IIPIMS seems to be the preferred acronym.

powers (up to 3000 W/cm^2 at a duty cycle of 0.5–5%) are used at low duty cycles to give an average power similar to continuous dc magnetron sputtering (e.g. 3 Wcm^2).[11,12] The advantage is that this waveform gives high ionization of metals in the plasma (up to 90%).[13] These "film ions" can have an appreciable lifetime in the plasma.[14] The disadvantage is that by only using a sharply peaked voltage pulse, the sputtering rate is lower than would normally be attained from continuous dc magnetron sputtering with the same power input probably due to the positive metal ions returning to the negative target.

By using a multistep waveform of about 2–4 ms duration, a high ionization of the vapor flux is attained as well as keeping the sputtering rate similar to dc magnetron sputtering (modulated pulse power (MPP)-HIPIMS or HIPIMS+).[15–18]

The question might be raised as to why, if there are so many film-ions formed, they aren't accelerated through the target potential, bombarding the sputtering target and giving "self-sputtering". A model indicates that in HIPIMS the maximum potential is established about 1 cm from the target surface. Ions formed near the target surface are accelerated away from the target.[19] No such potential reversal is found in a dc discharge.

5.4.5 Radio Frequency (rf) Capacitively Coupled Diode Discharge Plasmas

The rf extends from a few kilohertz to the high megahertz range. At the low end (e.g. 400 kHz), the rf is used for induction heating as well as plasma generation. Even though electrons and ions have differing masses (1 : 4000–100 000) at the low frequencies (<500 kHz) and in low pressure gases, both electrons and ions can follow the variations in electric fields. Above about 3 MHz the inertia of the ions prevents them from rapidly responding to changes in the electric field, whereas the electrons still rapidly follow the electric field. If the frequency is increased to above about 900 MHz, the electrons will be unable to follow the electric field variations.

In a capacitively coupled rf discharge, the electrons are caused to oscillate in the gas between the rf electrodes, thus gaining energy, as shown in Figure 1.2. The plasma acts as a low density electrical conductor and the rf field penetrates some distance into the plasma, thus generating ions and electrons throughout the space between the electrodes. In the rf diode system the plasma-generation region is primarily between the electrodes. At high frequencies the massive ions only respond to the time-averaged electric field (bias) while the electrons move to and away from the electrodes, creating high sheath potentials. The plasma will always be positive with respect to large-area electrodes and other surfaces.

Typically, low pressure rf sputtering systems operate at 13.56 MHz or at harmonics thereof,[c] with peak-to-peak voltages of greater than 1000 volts and power of up to 10 watts/cm^2 on

[c] The first time I tried rf sputtering I used an old diathermy machine (used to rf heat body tissue). After several months of use I got a visit from Federal Communications Commission (FCC) inspectors – it seems I was interfering with aircraft communication with the nearby airfield. That is why you need to have good rf shielding if you don't use a commercial frequency such as 13.56 MHz.

the electrodes.[20] The potential that appears at the surface of the driven electrodes in a parallel plate arrangement depends on the relative areas of the electrodes. In addition to the bias imposed by the rf field, a dc bias can be imposed on the surface by placing a blocking capacitor in the rf circuit or by having a dc potential applied from a dc source through an rf choke. If the area of the grounded walls in contact with the plasma is large, the plasma potential is determined by the grounded walls.

The conductance and capacitance of the discharge, and the rf potentials in the plasma volume, can be determined using capacitive probes. Typically, an rf discharge is established at 0.5–10 mTorr and has an electron density of 10^9–10^{11}/cm^3. The actual power input to the plasma is lessened by losses such as impedance mismatch, which causes power to be reflected back into the power supply and coupling to other surfaces in the system. Note that plasma shields, as used with dc discharges, cannot be used with an rf electrode because the rf couples into the shield. Keep all ground surfaces at least 10 Debye lengths from the rf electrode (i.e. the lower the pressure, the further away they should be). Horwitz (1983)[20] indicates a method of determining how much power is actually coupled into the plasma.

Impedance matching networks are used to couple the maximum amount of power into the plasma by reducing the reflected power. The matching network should be placed as close as possible to the rf electrode and connected to the electrode with low capacitance and low inductance leads. The matching networks can be manually tuned or self-tuned. Avoid ground loops in the electrical circuits; i.e., ensure that each power unit is independently tied to a common ground and not to another power unit.

Radio frequency-driven electrode surfaces immersed in a plasma assume a self-bias with respect to ground. This bias depends strongly on the electrode configurations and the capacitance in the circuit. For the case of the symmetric rf diode system, where the electrodes are of equal area and there is no capacitance in the circuit, the plasma potential is slightly more positive than the positive electrode. If, on the other hand, the electrode areas are unequal in size (e.g. one leg is grounded), there is a capacitance on one branch of the external electrode circuit and the rf circuit is asymmetric. In the asymmetric discharge, the electrode having the smaller capacitance (e.g. smaller area) has a higher negative potential with respect to plasma than the other electrode and it is bombarded with higher energy ions.

In capacitively coupled rf discharges, the plasma potential, and hence the sheath potential at the electrodes, can have a time-varying value of tens to hundreds of volts. When the electrodes have a different effective area, the plasma potential can also have a large dc potential with respect to one or more of the electrodes. These factors affect the distribution of ion energies incident on the electrode surfaces in an rf discharge. The electrode potentials can be varied using an external capacitance.

The frequency of the plasma discharge affects the dc sheath potential that is developed between the electrode and the plasma. When the rf electrode(s) are metal-backed insulators, the metal-insulator-plasma acts as a capacitor and the surface potential that appears on the insulator surface alternates between a low negative potential and a high negative potential with respect to the plasma. Energetic ions are extracted from the rf plasma due to the bias and may be used to bombard and sputter an insulator surface. The rf plasma can be operated at pressures as low as 0.5 mTorr in argon, though, at low pressures, high peak-to-peak voltages are required. If the electrode surface is to be a dielectric, it must completely cover the conductive electrode surface. If the metallic conductor backing plate is exposed, the "capacitor" is effectively shorted. This is a common problem in sputter cleaning and plasma treatment of dielectric surfaces where the dielectric surface is placed on the metal surface without completely covering it.

5.4.6 Arc Plasmas

Vacuum arc plasmas are formed by passing a low voltage–high current dc current arc between electrodes in a vacuum. This arc vaporizes electrode material, causing a plasma to form in the vapor between the two electrodes. In the arc, there is appreciable ionization of the material and many of the ions are multiply charged. It has been found that the ions from a vacuum arc have a high kinetic energy (50–75 eV for singly charged ions) due to a positive space charge formed above the cathode surface that accelerates the ions away from that region.

Gas arc plasmas are formed by passing a low voltage–high current dc current (arc) through a low pressure gas, which vaporizes electrode material and allows a plasma to form in the gas/vapor mixture between the cathode and the anode. In the arc, there is appreciable ionization of both the gas and the electrode material and many of the ions are multiply charged. Since there is a gas present, ions which are accelerated away from the space charge region may be thermalized by collisions. In film deposition, it is common to accelerate the gas ions and the film ions to a substrate using an applied negative potential on the substrate. Cathodic arc film deposition processes use a solid water-cooled cathode as the source of the depositing material while the anodic arc deposition process uses a molten anode for the vapor source.

5.4.7 Laser-Induced Plasmas

Lasers can be used to vaporize surfaces and the laser radiation passing through the vapor cloud can ionize a high percentage of the vapor. Laser vaporization is sometimes called laser ablation. Typically, an excimer laser (yttrium aluminum garnet (YAG) or argon fluoride (ARF)) is used to deposit energy in pulses. The YAG lasers typically deliver pulses (5 ns, 5 Hz) with an energy of about 1 J/pulse and the ARF lasers typically deliver pulses (20 ns, 50 Hz) with about 300 nJ/pulse. The deposited energy density can be greater than 5×10^{10} W/cm^2. The vaporized material forms a plume above the surface where some of the laser energy is adsorbed and ionization and excitation occur. In laser vaporization the ejected material is highly directed.

5.5 Ion and Plasma Sources

In much plasma processing, the surface being processed is in the plasma-generation region. In other cases, it is desirable to produce the plasma in a plasma source and process the surface away from the plasma-generation region. These plasma sources can provide the ions for bombarding the sputtering target in sputter deposition or the growing film in ion plating. They may provide the activated gaseous species desirable for reactive deposition processes or may provide dissociation of chemical vapor precursors to provide deposition from the vapor (e.g. $CH_4 \rightarrow C$). Using plasmas for processing is often desirable because the presence of both ions and electrons prevents charge buildup on dielectric surfaces.

5.5.1 Plasma Sources

The plasma generated in a plasma source can be confined magnetically to form a plasma beam.[21] In a plasma, the electrons are easily "steered" using a magnetic field and the ions follow to maintain charge neutrality. Plasma sources may be "gridless", which means that the particles in the beam have a spectrum of energies, or they may have extraction grids that allow more uniform ion energies.

End-Hall Plasma Source

In the Hall-effect plasma source, electrons are steered by a magnetic field to pass through a gas stream to an anode surface, as shown in Figure 5.9(a).[22] The gridless Hall-type plasma source is usually operated at rather low voltages (30–100 eV) and provides ions with a wide distribution of energies. This type of source is often used to provide an oxygen plasma for reactive deposition of oxides.

Hot Cathode Plasma Source

The Kaufman-type ion source[22] uses a thermoelectron emitter cathode, and grid-extraction to provide a ion source. The ion source is often used as a plasma source by injecting electrons into the ion beam after it has been extracted from the ion gun, as shown in Figure 5.9(b).

Capacitively Coupled rf Plasma Source

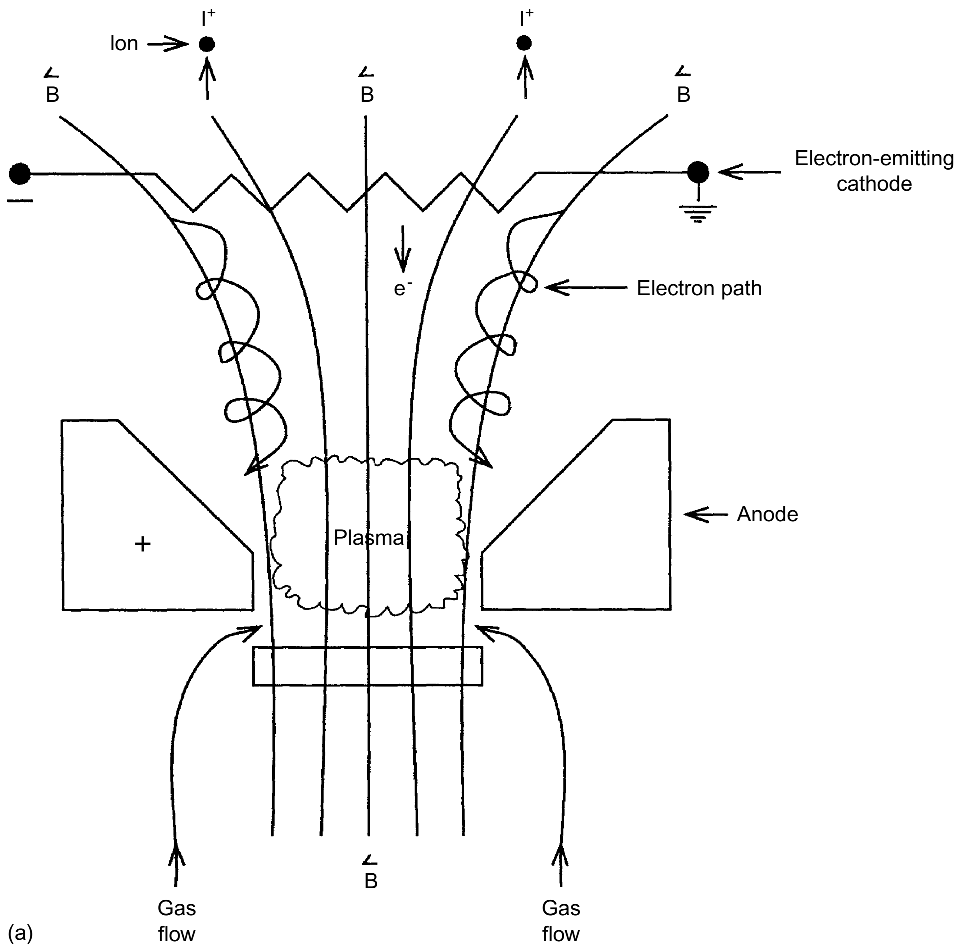
A parallel plate rf source can be used to form a linear plasma source, as shown in Figure 5.10(a). The rf frequencies typically range from 50 kHz–13.56 MHz.

Electron Cyclotron Resonance (ECR) Plasma Source

There is no sharp distinction between radio waves (rf) and microwaves, but typically microwaves are in the gigahertz (10^9 Hertz) range with a wavelength shorter than about

30 centimeters. A common industrial microwave frequency is 2.45 GHz. High frequencies (9.15 MHz–2.45 GHz) may be coupled with a magnetic field such that there is resonance coupling with circulating electrons to produce an electron cyclotron resonance (ECR) plasma.[23,24] In these discharges, a cavity resonator with an axially varying magnetic field is used to effectively couple microwave energy into electrons by resonant absorption. In the cavity, the electron density can be high (1 to $6 \times 10^{11}/cm^3$) and the electron temperature is relatively low (~10 eV) compared to the rf plasma. Figure 5.10(c) shows an ECR source.

The ECR discharge configurations may be of either a single pole (magnetic) cavity or a multipole (magnetic) cavity design. Single cavity systems form divergent fields. Multipole systems provide higher electron densities and a more uniform field over a large area. The ions from a multipole cavity are also more monoenergetic. The properties of an ECR plasma are very sensitive to reactor design. In order to spread the beam and maintain a uniform plasma density, a "plasma bucket" can be used.



(a)

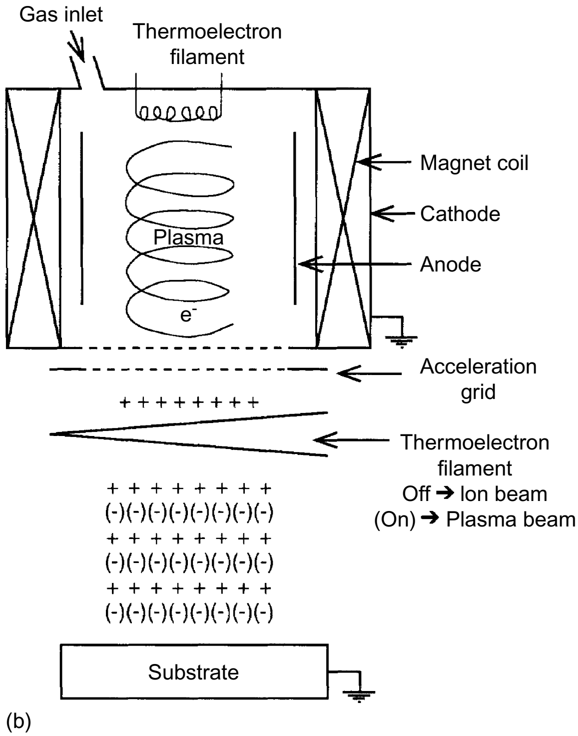


Figure 5.9: (a) End-Hall Plasma Source, (b) Kaufman Plasma Source

Typically, an ECR discharge is established at 1 kW, 2.45 GHz, 800–1000 gauss, and 0.1–10 mTorr gas pressure with an electron density of 10^{10}–10^{12} electrons/cm^3 and a self-bias (plasma potential) of 10–20 volts in the remote substrate position. Auxiliary magnetic fields may be used in the vicinity of the substrate to increase plasma uniformity over the substrate surface. The ECR sources suffer from the difficulty in scaling them up to large-area sources.

Inductively Coupled rf Plasma (ICP) Source

Inductively coupled gas discharges are formed using frequencies from 400 kHz to 5 MHz generally applied to a coil surrounding a quartz tube holding the plasma, which acts as a lossy conductor, as shown in Figure 5.10(b).[25] Inductively coupled sources are amenable to being scaled up to large-area sources with high plasma enthalpy. The rf coil can be internal to the chamber to give an immersed coil source.

Helicon Plasma Source

In the helicon plasma source, an rf-driven antenna radiates into a cylinder having a rather weak axial magnetic field, as shown in Figure 5.10(d). Resonant wave–particle interaction

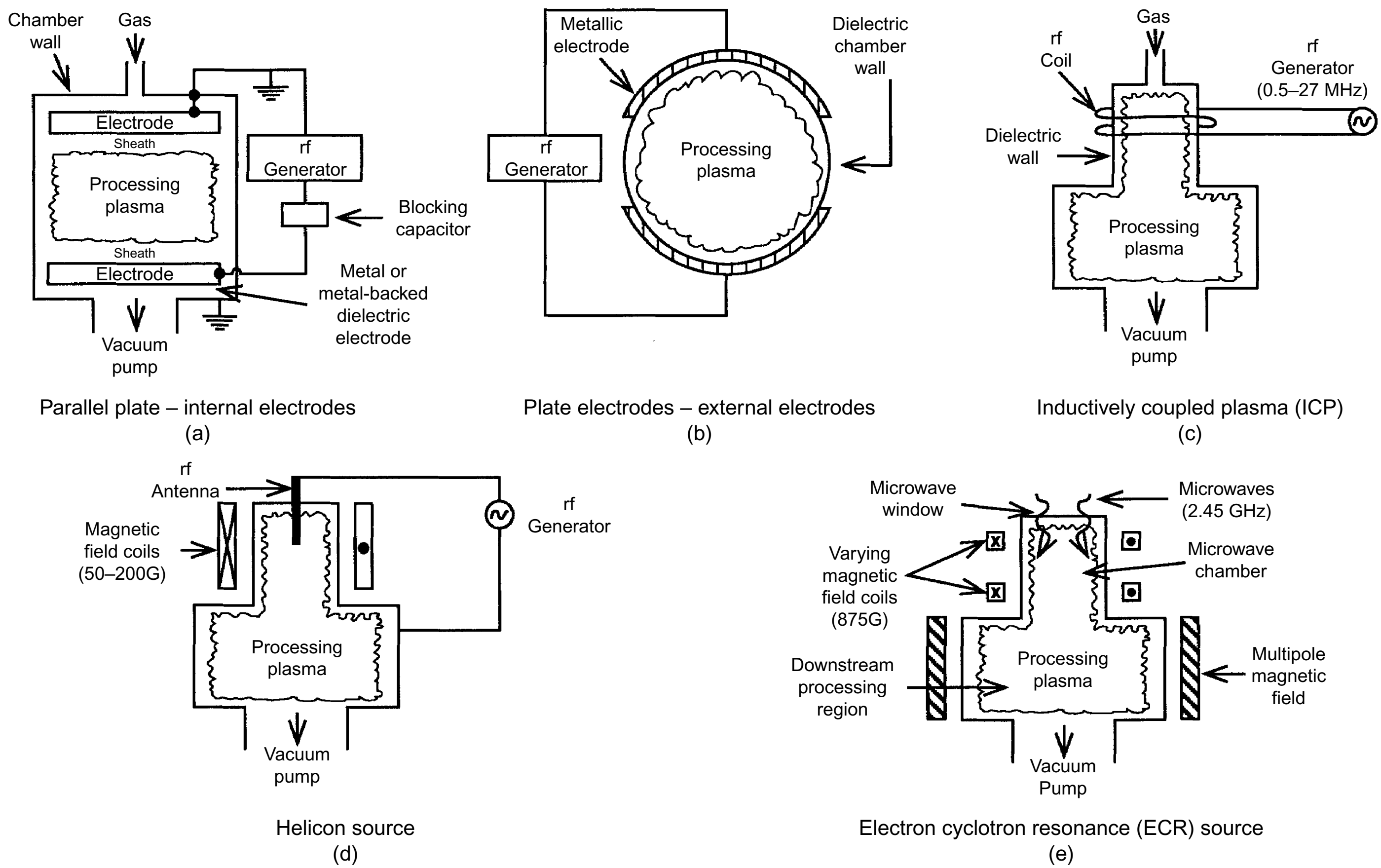


Figure 5.10: Plasma Sources: (a) Parallel Plate Radio Frequency (rf), (b) external (rf) electrodes (c) Inductively Coupled, (d) Electron Cyclotron Resonance (ECR) Discharge, (e) Helicon Discharge

transfers the wave energy to the electron. The helicon plasma source can also be configured as a linear array of antennae to form a rectangular ion source.

Hollow Cathode Plasma Source

A hollow cathode can be used as a plasma source. When arrayed in a line, hollow cathodes can form a linear plasma source. For example, a linear hollow cathode array using oxygen gas and magnetic confinement of the plasma has been used to clean oil from strip steel. It was found that a few per cent CF_4 in the plasma increased the cleaning rate.

5.5.2 Ion Sources (Ion Guns)

Ion sources produce pure ion beams. Typically, ions are produced in a plasma contained in a confined volume, and ions are extracted using a grid system, which confines the electrons and accelerates the ions. This configuration can be used to generate ion beams with a rather well defined energy distribution, and the source is called an ion gun. Ion gun sources allow the acceleration of ions to high energies in the grid structure; however, the grid limits the current density that can be extracted. The ion density (current) in an ion beam can be measured using a "Faraday cup".[26] Often, after extraction, low energy electrons are added to the ion beam to make a plasma beam (volumetrically neutral – space charge neutralization) to avoid coulombic repulsion in the beam ("space-charge blow up") and surface change buildup.

The plasma in the ion gun can be formed using a hot filament (Kaufman ion gun) (Figure 5.9b), an immersed rf coil, an external rf coil, or a resonant cavity such as an ECR source. Ion sources developed for the fusion reactor program are capable of developing fluxes of 10^{18}–10^{19} ions/cm^2/sec over hundreds of square centimeters of extraction area. Typical ion guns for semiconductor etching, ion beam sputtering, and ion-assisted processing give <10 ma/cm^2 over tens of square centimeters of area.

In gun-type ion sources, inert gas ions, and ions of reactive species, both gaseous (N^+, O^+) and condensable (C^+, B^+) ions, may also be formed and accelerated. Molecules containing the species to be deposited can be fragmented, ionized, and accelerated in the plasmas (e.g. SiH_4 can be fragmented, ionized, and accelerated to give deposition of a-Si:H, and CH_4 may be fragmented, ionized, and accelerated, and used to deposit carbon and diamond-like carbon (DLC) films).

Sources for forming ions of condensable species (film ions) in vacuum began with the development of ion sources for isotope separation using mass spectrometers such as the Calutron in the 1940s[27,28] and continues in the present.

5.5.3 Electron Sources

Electrons are used to heat surfaces and to ionize atoms and molecules. The most common source of electrons is a hot electron (thermoelectron)-emitting surface. Generally, the electron emitter is a tungsten or thoriated tungsten filament. Lanthanum hexaboride or La–Mo electron emitter surfaces can provide a higher electron emission for a given temperature than can tungsten.

Plasma sources are often used as electron sources by magnetically deflecting the electrons. The hollow cathode electron source uses a plasma discharge in a cavity having a negative potential on its walls that reflects and traps electrons, thus enhancing ionization in the cavity. If the discharge in the cavity is a glow discharge and the walls are kept cool, the hollow cathode is called a cold hollow cathode and runs at relatively high voltage and low currents. If the discharge is supported by thermoelectrons emitted from the hot walls, it is called a hot hollow cathode and operates in an arc mode with low voltages and high currents.

In the cold hollow cathode source there is an anode grid surrounded by a cathode chamber. A dc discharge is established and an orifice allows the plasma beam to exit from the chamber. The discharge can also be operated using a hot filament in the anode chamber and augmented by a magnetic field.

In a hot hollow cathode source, the gas pressure in a tube is raised by having an orifice restricting the exit of gas from the tube and the thermoelectrons are trapped in the anode cavity.[29] A high density plasma beam exits the orifice and the electrons may be used to evaporate material or ionize gases. The hot hollow cathode is capable of much higher electron and ion densities than the cold hollow cathode system. The hollow cathode electron source can be used to augment plasma generation.

5.6 Plasma Processing Systems

A good plasma system must first be a good vacuum system since contaminants will be activated in the plasma. In comparison to vacuum processing systems, plasma processing systems are complicated by:

- High gas loads from the introduction of processing gases.
- Often, a reduced pumping speed (gas throughput) in the deposition chamber.
- The potentially explosive or flammable gases that are used in some plasma-based processes.

In many cases the generalized vacuum processing system shown in Figure 3.8 may be used with a plasma in the processing chamber if the pumping system and fixturing is designed appropriately. Flow control, for establishing the gas pressure needed to form a plasma, can be done by partially closing (throttling) the high vacuum valve, by using a variable conductance valve in series with the high vacuum valve, or by the addition of an optional gas flow path as indicated. The electrode for forming the plasma ("glow bar") is positioned so as to extend into as large a region of the chamber as possible (Sec. 13.11.1).

In plasma processing, the deposition conditions differ greatly, depending on whether the substrate is placed on an active electrode, in the plasma-generation region, or in a "remote position" where the plasma afterglow is found.

Plasma-based processes may either be clean or "dirty". Sputter deposition and ion plating are generally relatively clean processes, while plasma etching and PECVD are dirty processes. The main equipment-related problems in plasma-based PVD processing are:

- Production of a plasma having desirable and uniform properties in critical regions of the processing volume.
- Control of the mass flow rate and composition of the gases and vapors introduced into the system.
- Removal of unused processing gases, reaction products, and contaminant gases and vapors from the processing volume.
- Prevention of charge buildup and arcing.
- Corrosion if corrosive gases or vapors are used in the processing.

5.6.1 Electrodes

Electrodes in a plasma system are important in determining the plasma properties. For dc potentials, corners, edges, and points are high field regions. The curvature of the equipotential surfaces in such regions affects the acceleration of ions and electrons, as shown in Figure 5.4. High transmission grids ($>$50%) can be used in plasma systems to establish the position of equipotential surfaces, as shown in Figures 5.4 and 3.13(f).

For rf potentials, the electrodes act as antenna, broadcasting the electric field into the space around the electrode. The radiation pattern from the electrode is affected by its shape and shape is more important at the higher rf frequencies. This means that the plasma generation by the electrode is affected by its shape. The best electrode shapes are simple surfaces, for example a flat plate. Complex surfaces may have to be surrounded by an open grid structure in order to attain a uniform radiation pattern and more uniform plasma generation. In some cases, it is desirable to prevent rf power from being coupled into a surface or into a region around a surface. The surface can be placed inside a metallic grid, which forms a field-free region around the surface. This configuration is like the "etch tunnel" used in plasma etching.

5.6.2 Corrosion

Corrosion can be a problem in plasma systems that use corrosive or potentially corrosive processing gases. Corrosion can produce particulate contamination in the system as well as destroy sealing surfaces. It is a particular problem when using stainless steel or aluminum in the presence of chlorine. Pumps should be designed and built to handle corrosive gases/vapors and particulates. If corrosive gases and/or particulates are being pumped, the pump oils should be compatible with the gases/vapors and should be routinely changed.

Heavily anodized aluminum is used in plasma systems exposed to chlorine plasmas, which corrode stainless steel. After anodization, the anodized layer is densified by "sealing" using hot water containing nickel acetate or, if heavy metal contamination is a concern, steam sealing can be used. The Hastalloy™ C-22 alloy is also used for chlorine environments. Monel™ and polymer-coated surfaces are used in some applications.

5.6.3 Pumping Plasma Systems

Pumping in plasma systems can be done with any pump that can operate at the desired flow rate and pressure, that is compatible with the gases being used, and that can handle the contaminants generated. Typical flow rates for plasma cleaning, sputter deposition, and ion plating are about 200 sccm.

5.7 Plasma-related Contamination

Plasma can be effective in forming, releasing, and activating contamination in the vacuum system. If low gas throughput is being used, the contaminant gases, vapors, and particulates are not readily pumped away. In order to aid in the removal of the contaminants, a "pump, discharge, flush, pump" sequence can be used. In this operation, the system is pumped down to a low pressure, the conductance is decreased, and the pressure is raised so that a discharge can be established. The gas discharge desorbs the contaminants and when the pumping system is opened to full conductance the contaminants are pumped out of the system.

5.7.1 Desorbed Contamination

Plasmas enhance desorption from surfaces by ion scrubbing, photodesorption, and heating of surfaces due to radiation and recombination. Inert gas plasmas are used to desorb (ion scrub) contaminants such as water vapor. Reactive gases such as oxygen and hydrogen are used to chemically react with and volatilize contaminants such as hydrocarbons.

5.7.2 Sputtered Contamination

High energy neutrals that are reflected from the cathode or formed by charge exchange processes can cause sputtering in undesired locations when there are low gas pressures in the plasma system. Contamination from fixtures, shutters, and other surfaces can occur. For example, if a stainless steel shield is used around a gold sputtering target, the stainless steel will be sputtered and contaminate the gold film. In some cases, the surface being sputtered can be coated with the material being deposited so the sputtered "contaminant" is of the film material. Dielectric or electrically floating surfaces can attain a high enough self-bias in the plasma system to be sputtered by ions accelerated from the plasma.

5.7.3 Arcing

Arcs can vaporize material and generate particulates in the plasma system. Arcing generally occurs over surfaces when a potential difference has been established due to plasma conditions. Arcing is particularly bad when depositing electrically insulating or poorly conducting films. Arcing can often be minimized by using pulsed dc rather than continuous dc or by adding an rf component to the dc plasma power source. Arcing can also occur over the electrical insulators in the feedthroughs if the insulators are coated by deposited film material. The feedthroughs should be shielded from depositing film material.

5.7.4 Vapor Phase Nucleation

Plasma-based PVD processing can produce ultrafine particles ("soot" or "black sooty crap" (BSC)) in the plasma region by vapor-phase nucleation, thereby generating a "dusty plasma".[30] This is particularly true when using hydrocarbon precursors in the reactive deposition of carbides. These particles attain a negative charge and are suspended in the plasma near walls where they can grow to appreciable size.

Since the walls are also at a negative potential with respect to the plasma, particles will be suspended in the plasma. These particles can be monitored using scattered laser light techniques. Since the particles in the plasma have a negative charge, they will not deposit on the negatively biased or grounded surfaces during deposition but will deposit on the chamber walls and the substrates when the plasma is extinguished and the self-bias disappears. These particulates should be swept through the vacuum pumping system as much as possible. This is best done by keeping the plasma on and opening the conductance valve to extinguish the plasma by rapidly reducing the pressure. The applied bias potential on surfaces should be retained until the plasma is extinguished. These particles can clog screens (such as the one over the inlet of a turbo pump) and accumulate in pump oils, and the oils should be changed periodically.

5.7.5 Cleaning Plasma Processing Systems

Plasma systems are cleaned the same way as vacuum systems are cleaned. Removable shields and liners should be used wherever possible. Plasma systems used for PVD processing may have a large number of particulates generated during the processing from vapor phase nucleation, arcing, and flaking. Particulates should be removed using a dedicated vacuum cleaner with a HEPA-type filter system.

In some cases, the plasma system can be cleaning using *in situ* plasma etching (Sec. 13.11). For example, when nitrides have been deposited in the system, the system can be cleaned using a plasma containing CF_4 or NF_3, which produce a lot of fluorine radicals. Oxygen plasmas can be used to remove carbon and hydrocarbon contamination from the system.

5.8 Some Safety Aspects of Plasma Processing

Plasmas are electrical conductors and the presence of a high voltage anywhere in the system can allow un-grounded surfaces in contact with the plasma to attain a high voltage. For example, a metal chamber isolated from ground by a rubber gasket can attain a high potential if an ionization gauge is used in contact with the plasma. Make sure that all metal surfaces that are not meant to be electrodes are grounded in a plasma system.

There have been several explosions in plasma pumping systems when people have tried to pump pure oxygen through a system containing hydrocarbon pump oils. Compressing the pure oxygen in contact with the hydrocarbon oil is like making it into a diesel engine. Vacuum pumps are not designed to be internal combustion engines. When pumping oxygen, make sure that the pump oils are compatible with oxygen or use a less-explosive oxygen mixture such as air. Hydrogen is extremely explosive and flammable and should be pumped with care. Forming gas, which is a mixture of hydrogen in nitrogen (1 : 9), is less dangerous than pure hydrogen.

When pumping some processing gases and vapors, the gases/vapors can accumulate in the pump oils, decreasing their performance and perhaps presenting a safety hazard during maintenance and repair. In plasma etching, where relatively high gas pressures are used and numerous species can be formed in the plasma, care should be taken with the pump oil and exhaust since some of the species formed may be toxic, mutagenic, or carcinogenic. For example, if CCl_4 has been pumped in the presence of water vapor, phosgene ($COCl_2$), a highly toxic chemical warfare agent, can be produced and accumulate in the pump oil.

Concern has been expressed about the possibility of producing cyanide gas when using nitrogen and a hydrocarbon vapor in the reactive deposition of carbonitrides, but no evidence of significant levels of cyanide gas has ever been detected to my knowledge.

5.9 Summary

In PVD processing a plasma is used as a source of ions and electrons as well as to activate reactive species for reactive deposition processes. Plasmas are generated by electron–ion collisions giving ionization, but there are many configurations for generating and using plasmas. Typically, one of the goals in plasma generation is to generate as highly ionized a plasma as possible at a low gas density. This often involves using magnetic fields to control the path of electrons in the low pressure gas. Another goal is to generate a uniform plasma in the processing volume. A good plasma system should first be a good vacuum system since contaminants are activated in the plasma.

References

[1] D.M. Mattox, The historical development of controlled ion-assisted and plasma-assisted PVD processes, in: Proceedings of the 40th Annual Technical Conference, Society of Vacuum Coaters, 1997, p. 109.

[2] A.N. Chester, Gas pumping in discharge tubes, Phys. Rev. 169 (1) (1968) 172.

[3] D.W. Hoffman, A sputtering wind, J. Vac. Sci. Technol. A3 (1985) 561.

[4] G. Lucovsky, D.V. Tsu, R.J. Markunas, Formation of thin films by remote plasma enhanced chemical vapor deposition (remote PECVD), in: S.M. Rossnagel, J.J. Cuomo, W.D. Westwood (Eds.), Handbook of Plasma Processing Technology: Fundamentals, Etching, Deposition and Surface Interactions, Noyes Publications, 1990, Chapter 16.

[5] J.A. Thornton, Diagnostic methods for sputtering plasmas, J. Vac. Sci. Technol. 15 (2) (1978) 188.

[6] R.W. Dreyfus, J.M. Jasinski, R.E. Walkup, G.S. Selwyn, Optical diagnostics of low pressure plasmas, Pure Appl. Chem. 57 (9) (1985) 1265.

[7] D.M. Mattox, Surface effects in reactive ion plating, Appl. Surf. Sci. 48/49 (1991) 540.

[8] J.E. Brittain, The magnetron and the beginnings of the microwave age, Phys. Today 38 (7) (1985) 60.

[9] T.A. Beer, J. Laimer, H. Störi, Study of the ignition behavior of the dc discharge used for plasma-assisted chemical-vapor deposition, J. Vac. Sci. Technol. A18 (2) (2000) 423.

[10] V. Kouznetesov, Method and Apparatus for Magnetically Enhanced Sputtering, US Patent 6 296 742 B1 (09.12.1997).

[11] L. Bohlmark, J. Almi, C. Christov, A.P. Ehiasarian, Ionization of metals in high power pulsed magnetron sputtering, J. Vac. Sci. Technol. A23 (2) (2005) 18.

[12] P. Sigurjonsson, P. Larsson, D. Lundin, U. Helmersson, J.T. Gudmundsson, Langmuir study of plasma parameters in the HiPIMS discharge, in: Proceedings of the 52nd Annual Technical Conference, Society of Vacuum Coaters, 2009, p. 234.

[13] V. Kouznetsov, K. Macak, J.M. Schneider, U. Helmersson, I. Petrov, Surf. Coat. Technol. 122 (1999) 290.

[14] A. Hecimovic, A.P. Ehiasarian, Spatial and temporal evolution of ion energies in HIPIMS plasma discharge, in: Proceedings of the 52nd Annual Technical Conference, Society of Vacuum Coaters, 2009, p. 240.

[15] R. Chistyakov, Method and Apparatus for Generating Strongly Ionized Plasmas with Ionizational Instabilities, US Patent 7 095 179 (22.08.2006).

[16] R. Chistyakov, High-power Pulsed Magnetron Sputtering, US Patent 7 147 759 (12.12.2006).

[17] R. Chistyakov, B. Abraham, High power pulse plasma generator for modulated pulse power sputtering processes, in: Proceedings of the 51st Annual Technical Conference, Society of Vacuum Coaters, 2008, p. 321.

[18] R. Chistyakov, B. Abraham, Pt. 1 & Pt. 2 – Advanced pulsed dc technology for material processing applications, in: Spring Bulletin and p. 32 in Summer Bulletin, Society of Vacuum Coaters, 2009, p. 46 (<svc.org/Publications/SVC-Bulletin-Recent-Issues>).

[19] N. Brenning, I. Axnäs, M.A. Raadu, D. Lundin, U. Helmersson, A bulk plasma model for dc and HIPIMS magnetrons, Plasma Sources Sci. Technol. 17 (2008) 045009.

[20] C.M. Horwitz, Radio frequency sputtering – the significance of power input, J. Vac. Sci. Technol. A1 (1983) 1795.

[21] A.M. Dorodnov, Technical applications of plasma accelerators, Sov. Phys. Tech. Phys. 23 (1978) 1058.

[22] H.R. Kaufman, R.S. Robinson, Broad-beam ion sources, in: S.M. Rossnagel, J.J. Cuomo, W.D. Westwood (Eds.), Handbook of Plasma Processing Technology: Fundamentals, Etching, Deposition and Surface Interactions, Noyes Publications, 1990, Chapter 7.

[23] M.A. Liberman, R.A. Gottscho, Design of high-density plasma sources, in: M.H. Francombe, J.L. Vossen (Eds.), Plasma Sources for Thin Film Deposition and Etching, Vol. 18 in series Physics of Thin Films, Academic Press, 1994, p. 1.

[24] J. Assmussen, Electron cyclotron resonance microwave discharges for etching and thin film deposition, in: S.M. Rossnagel, J.J. Cuomo, W.D. Westwood (Eds.), Handbook of Plasma Processing Technology: Fundamentals, Etching, Deposition and Surface Interactions, Noyes Publication, 1990, Chapter 11.

[25] D.E. Hull, Induction Plasma Tube, US Patent 4 431 901 (14.02.1984).

[26] D. Gardner, W. Sainty, Ion current measurement and ion beam neutralization using a novel Faraday Cup operable during deposition, in: Proceedings of the 50th Annual Technical Conference, Society of Vacuum Coaters, 2007, p. 534.

[27] J. Druaux, R. Bernas, Electromagnetically Enriched Isotopes and Mass Spectrometry, M.L. Smith (Ed.), Academic Press, 1956.

[28] L. Valyi, Atom and ion sources, John Wiley, 1977.

[29] Y.S. Kuo, R.F. Bunshah, D. Okrent, Hot hollow cathode and its applications in vacuum coating: a concise review, J. Vac. Sci. Technol. A4 (3) (1986) 397.

[30] C.S. Selwyn, R.S. Bennett, In-situ laser diagnostics studies of plasma-generated particulate contamination, J. Vac. Sci. Technol. A7 (4) (1989) 2758.