Chapter 2

The Glow Discharge

2.2 Introduction

The term "plasma" was first introduced by Irving Langmuir (1881–1957) in the 1920's. The behavior of low pressure DC electrical discharges in gases was studied by many English and German physicists during the 19th century. They developed various evacuated tubes to illustrate the strange behavior of the plasma.

Electrons and ions are charged particles, they can be preferentially heated by applying an electric or magnetic field to the plasma, keeping the neutral gas atoms at a low temperature. Most notably, electrons with low mass are easily accelerated to energies for ionization of the gas atoms, with typical values of kinetic energy in the 1-10 eV range (equivalent to ~10^4-10^5 K). Due to the low gas temperatures of electrical discharge plasmas, they are sometimes also referred to as cold plasmas. Obviously, electrical discharge plasmas are not in thermal equilibrium, since $T_e >> T_g$ and $T_e > T_i > T_g$ [6].

The two most common types of electrically induced plasmas are the direct-current glow discharge, and the radio-frequency discharge, where a radio-frequency electric field is coupled either capacitively or inductively to the electrons of the discharge [6].

2.2. Brief History of Glow Discharge

The scientific examination of the glow discharge started during the latter half of the 19^{th} century and was closely related to advances in vacuum technology. When high potentials were obtainable together with means of pumping air out of closed glass vessels, it was observed that the high-voltage electric spark between two electrodes produced a variety of colourful and silent ribbon-like discharges as the gas pressure was progressively reduced. In 1944, Faraday discovered that, as the gas pressure was reduced, the luminosity receded towards the anode of a discharge tube, leaving a dark space, demonstrating the existence of a dark discharge of electricity in gases.

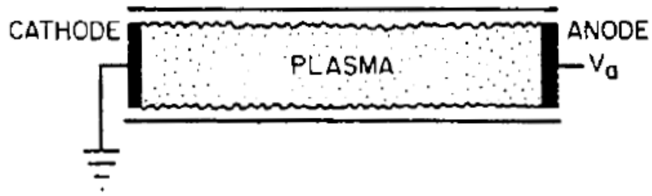
Development of electrode material, and technical advances in electrode and glass- / quartz-tube constructions have played an important role in the investigation of various forms of glow discharges [7]. In the mid of 19^{th} century, Geissler introduced a mercury pump and developed a technique for constructing glass discharge tubes with metal electrodes inside (1858-60). Plucker (1858) noticed the glass in the vicinity began to phosphoresce, as the gas pressure was reduced. Throughout the following 25 years, investigations of the cause of this effect were carried out by Crookes, Hittorf, Glodstein and Hertz. In 1895, Rontgen discovered X-rays, and the work of J. J. Thomson using discharge tubes at low gas pressures ($\leq 10^{-4}$ mmHg) led to the discovery of the electron, and the measurement of the ratio of the charge to mass. Following that, J. J. Thomson and F.W. Aston developed the mass spectroscopy of ions, after the discovery that ‘positive rays’ could be passed from a glow discharge through a hole in the cathode. Thus, research into understanding of glow discharge played a vital role in the opening up of modern physics [7].

Today, glow discharges have been utilized in a wide range of practical applications. With much research and development, glow discharges are now not only being operated at low pressures, but also at high pressures up to atmospheric pressure without needing a vacuum system.

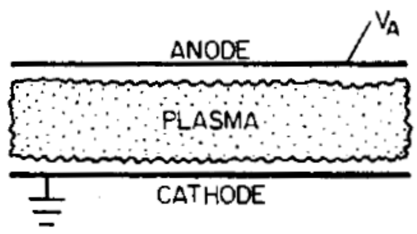
2.3 Introduction to Glow Discharge and Applications

The glow discharge owes its name to the fact that the plasma is luminous. This luminosity is produced because the electron energy and number density are high enough to generate visible light by recombination and excitation collisions [8].

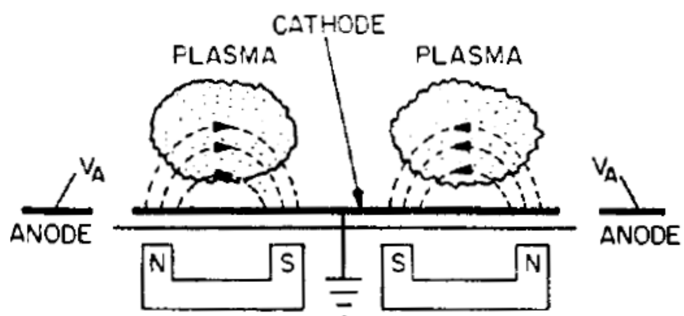
Glow discharges are used in a large number of applications. The light emitting character of glow discharge has several applications such as in the light industry (the classical electrical discharge tube used in fluorescence lamps, neon discharge tube for advertisements, etc.), as the pump source for gas lasers, and as flat plasma display panels for the new generation of flat, large area television screens. Besides, there are other important applications such as those in the microelectronic industry and in the material processing technology. These include surface treatment, etching of surfaces (for the fabrication of integrated circuits, etc.), plasma polymerisation, plasma modification of polymers, and the deposition of thin protective coatings. Other forms of glow discharge for industrial applications are such as DC parallel plate plasma reactors, electron bombardment plasma sources, etc. [8, 9]. Some of the common configurations of the glow discharge used in industry are shown in Figure 2.1.



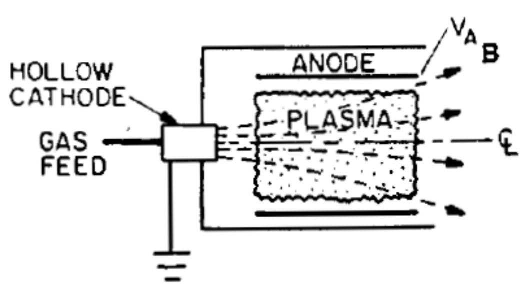
(a) Classical DC Electrical Discharge Tube



(b) Parallel Plate Plasma Reactor



(c) Coplanar Magnetron Reactor



(d) Coaxial Electron Bombardment Discharge Chamber

Figure 2.1: Various forms of the DC Glow Discharge [8]

In the simplest case, glow discharge is formed by applying a potential difference (of a few 100 V to a few kV) between two electrodes that are inserted in a cell or chamber filled with gas (an inert gas or a reactive gas) at a pressure ranging from a few mTorr to atmospheric pressure [9]. Due to the potential difference, the electrons are accelerated away from the cathode, and increase the collisions with the gas atoms and molecules. The collisions may produce processes such as excitation, ionization, dissociation, etc.. The excitation collisions create excited species, which can decay to lower levels by the emission of light, and this is responsible for the characteristic name of the "glow" discharge. The ions are accelerated toward the cathode, and they release secondary electrons when bombarding at the cathode surface. These secondary electrons are accelerated away from the cathode and they can give rise to more ionization collisions. Ionization collisions create ion-electron pairs, and this ion-electron multiplication process makes glow discharge a self-sustained plasma [9].

2.4 Different Types of Glow Discharge

There are various types of glow discharge plasmas. The basic version described above is the *direct current (dc) glow discharge*. A continuous potential difference is applied between the cathode and anode, producing a constant current. This setup may give rise to problems when one of the electrodes is non-conducting, as due to the constant current, the electrodes will be charged up and leading to burn-out of the glow discharge [9].

The problem in DC glow discharge is overcome by applying an alternating voltage between the two electrodes, such as in the *capacitively coupled radio-frequency (cc rf) glow discharge*. In this case, the charge accumulated during one half of the cycle, will be neutralized by the opposite charge accumulated during the next half-cycle [9].

An alternating current applied across the electrodes will give rise to an *alternating current (ac) glow discharge*. This can be considered as a consecution of short discharges, where the role of cathode and anode is changed alternately. One of the important ac glow discharge, operating at atmospheric pressure, is the *dielectric barrier discharge (DBD)*, in which the electrodes are typically covered by a dielectric barrier [9].

The glow discharge may also be operated by using a pulsed current source. This is the *pulsed glow discharge*, which consists of short glow discharges (with time lengths typically in the milli- or microsecond range), followed by an afterglow, which is generally characterized by a longer time-period. The advantage of this type of discharge is that for a low average power, high peak electrical power can be reached, resulting in high peak efficiencies for various applications [9].

A magnetic field can also be applied to a glow discharge besides applying a potential difference (or an electric field). The *magnetron discharge* is a well-known discharge type with crossed magnetic and electric fields. In the magnetron discharge, the electrons circulate in helices around the magnetic field lines and creating more ionisation. Hence, they are typically operated at lower pressures and higher currents as compared to the conventional glow discharges.

Several new discharge types characterized by low pressure and high plasma densities have also been developed. Their major difference from the conventional glow discharge is that the electrical power is applied by electromagnetic induction, not by application of a potential difference between the two electrodes as in the conventional type. This is the *inductively coupled discharge*, where the RF power is inductively coupled to the plasma. Another type of glow discharge is produced by using microwave power. The combination of the microwave discharge and a magnetic field gives rise to the *electron cyclotron resonance (ECR) reactor* [9].

2.5 DC (Direct Current) Glow Discharge

The DC glow discharge has been historically important, both in applications and in studying the properties of the plasma medium. For studying the glow discharge, the usual configuration is a long glass cylinder with anode electrode at one end and cathode electrode at the other end. The usual pressure range of operation is 10 mTorr to 10 Torr, and the typical voltage is a few hundreds volts between cathode and anode to maintain the discharge [10]. The parameter ranges of glow discharges are summarized in Table 2.1.

Table 2.1: Characteristic parameter ranges of DC Glow Discharge [8]

Parameter	Low Value	Characteristic Value	High Value
Neutral gas pressure (Torr)	10^{-6}	0.5	760
Electrode voltage (V)	100	1000	50 000
Electrode current (A)	10^{-4}	0.5	20
Number density (electrons/m^3)	10^{14}	5×10^{15}	6×10^{18}
Electron kinetic temperature (eV)	1	2	5
Power level (W)	10^{-2}	200	250 000
Plasma volume (liters)	10^{-6}	0.1	100

As the voltage across the classical DC low pressure electrical discharge tube is increased through the dark discharge region shown in the Figure 2.2, the current increases exponentially in the Townsend discharge region. When one approaches the breakdown voltage at the point E, and if the internal resistance of the power supply is relatively low, the gas will break down at the voltage V_B. Then the discharge will move from the dark region into the normal glow discharge region [8].

The glow discharge region is shown in greater details in Figure 2.3. The region from F to G is called the normal glow discharge. In this region, the voltage is relatively independent of the total current flowing in the discharge tube, and the current density reaching the electrode is also relatively independent of the total current. This means that the plasma is in contact with only a small part of the cathode surface at low current in the normal glow discharge region. The contact surface fills more and more of the total cross section of the cathode as the current increases, until at the point G, the boundary of the abnormal glow, the plasma covers the entire surface of the cathode, in order to deliver the required total current at a constant current density. In the abnormal glow discharge region, the voltage increases significantly with increasing total current, in order to force the cathode current density above its natural value and provide the desired current. The electrodes become sufficiently hot that the cathode emits electrons thermionically at point H. Then the discharge will undergo a glow-to-arc transition, if the DC power supply has a sufficient low internal resistance [8].

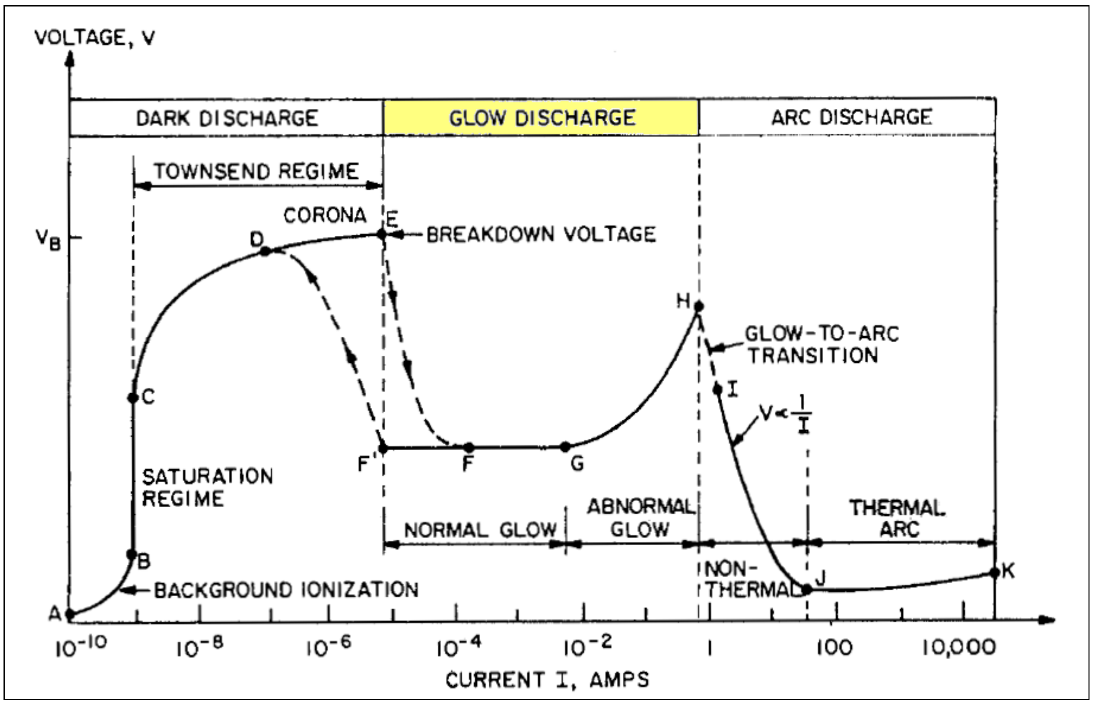


Figure 2.2: Voltage-Current characteristic of the DC low pressure electrical discharge [8].

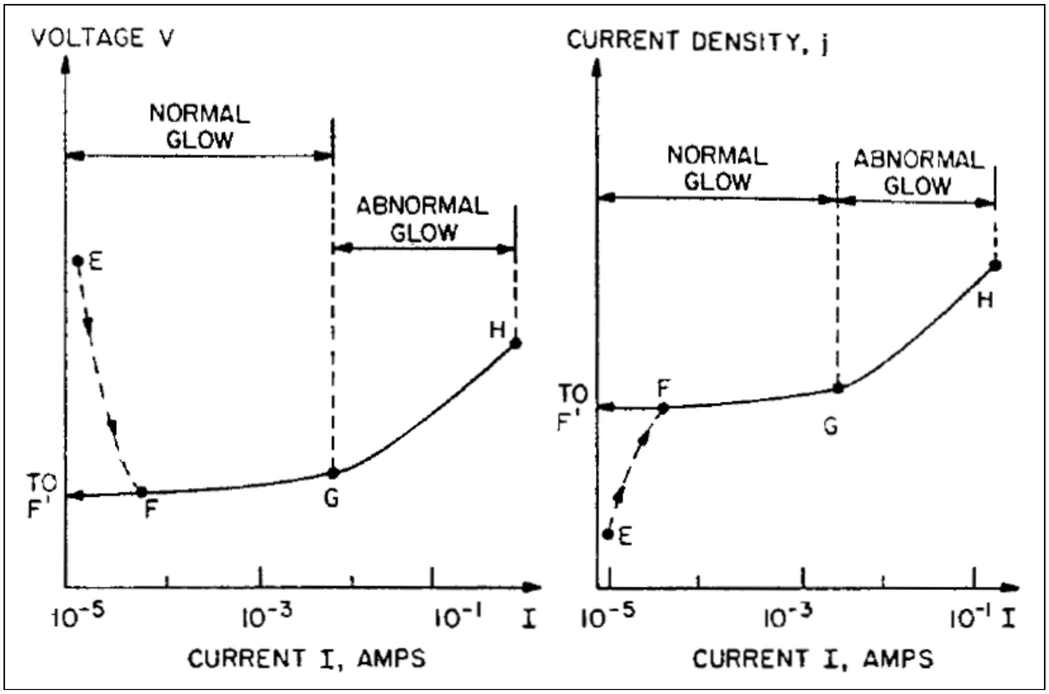


Figure 2.3: The variation of voltage and current density with current of a normal glow discharge [8].

2.6 The Qualitative Characteristics of Normal Glow Discharge

A classical electrical discharge in the normal glow region has the characteristics shown in Figure 2.4. The structures of Figure 2.4 (a) were first observed in the 1830's by Michael Faraday. The characteristic of the normal glow discharge received individual names, often in honor of the 19th century investigators who were among the first to observe or investigate them [8]. The appearance of the glow discharge can be identified into various regions as described below:

2.6.1 The Cathode

The secondary electron emission at the cathode surface plays a significant role in a self-sustaining glow discharge. The Townsend theory of gas discharge considers the ion bombardment at the cathode surface as a secondary source of electrons and defines the secondary electron emission coefficient as the number of electrons emitted from the cathode per ion bombardment. With the inclusion of this secondary source of electrons, the current density is described by [8]

$$J = \frac{J_0 e^{\alpha d}}{1-\gamma(e^{\alpha d}-1)} \qquad (\mathrm{A/m^2}) \;. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots...(2.1)$$

This leads to the condition of electrical breakdown and subsequently the self-sustained glow discharge.

2.6.2 Aston dark space

A thin region immediately in front of the cathode with a strong electric field and negative space charge is called the Aston dark space. It contains slow electrons which are in the process of being accelerated from the cathode. The electrons are of too low in density and energy to excite the gas, so it appears dark [8]. As it has negative space charge, which means that the initial stray electrons plus the secondary electrons, outcome the ions in this region [11].

2.6.3 Cathode glow

The next region is the cathode glow, which has a relatively high ion density. In this region, the electrons are energetic enough to excite the neutral atoms they collide with. It is often reddish or orange in colour due to the emission by excited atoms or incoming positive ions which are moving toward the cathode, sputtered off the cathode surface. The axial length of cathode glow region depends on the type of gas and the pressure. The cathode glow sometimes clings to the cathode and masks the Aston dark space [8].

2.6.4 Crookes (or Hittorf) dark space / Cathode fall

The region after the cathode glow is the Crookes dark space. It is the region over which most of the voltage drop occurs and has moderate electric field. This region has a positive space charge and relatively high ion density [8, 10].

2.6.5 Negative glow

This region has the brightest intensity in the entire discharge. It is the most intense on the cathode side and has relatively low electric field. The negative glow is usually longer than the cathode glow, and the electrons carry almost the entire current in this region. Here the electrons that have been accelerated through the cathode region produce ionization and intense excitation, hence the bright light output observed. Energy for excitation is no longer available as these electrons slow down, and the

Faraday dark space begins. The electron number density in the negative glow region is about 10^{16} electrons/m^3 [8].

2.6.6 Faraday dark space

The electron energy is low, and the electron number density decreases by recombination and diffusion to the walls in this region. The net space charge is very low and the axial electric field is relatively small [8].

2.6.7 Positive Column

This region is quasi-neutral as what Irving Langmuir had in mind when he defined plasma. The electric field is small in this region, typically 1 V/cm, and it is just large enough to maintain the required degree of ionization at its cathode end. The length of the positive column region can be varied by changing the distance between electrodes at a constant pressure and constant voltage drop, while the other regions maintain their lengths. The electron number density in the positive column is typically 10^{15} to 10^{16} electrons/m^3, with electron kinetic temperature of 1 to 2 eV. The positive column is a long, uniform glow, except when standing or moving striations are triggered spontaneously, or ionization waves are triggered by a disturbance. For a glow discharge in air, the positive column plasma is pinkish to blue [8, 10].

2.6.8 Anode glow

The anode glow is a bright region which is slightly more intense than the positive column. It is at the right end of positive column and is not always present. This is the boundary of the anode sheath [8].

2.6.9 Anode dark space

The anode dark space is the space between anode glow and the anode itself. It is the anode sheath which has a negative space charge due to electrons traveling from the positive column to the anode. The electric field in the anode dark space is higher than the positive column. The anode pulls electrons out of the positive column, acts like a Langmuir probe in electron saturation [8].

The characteristic axial profiles of the light intensity, potential distribution, field strength, net space charge, negative charges, and positive charges are shown in Figure 2.4 (b) with the visible structures to which they correspond indicated by Figure 2.4 (a) [8].

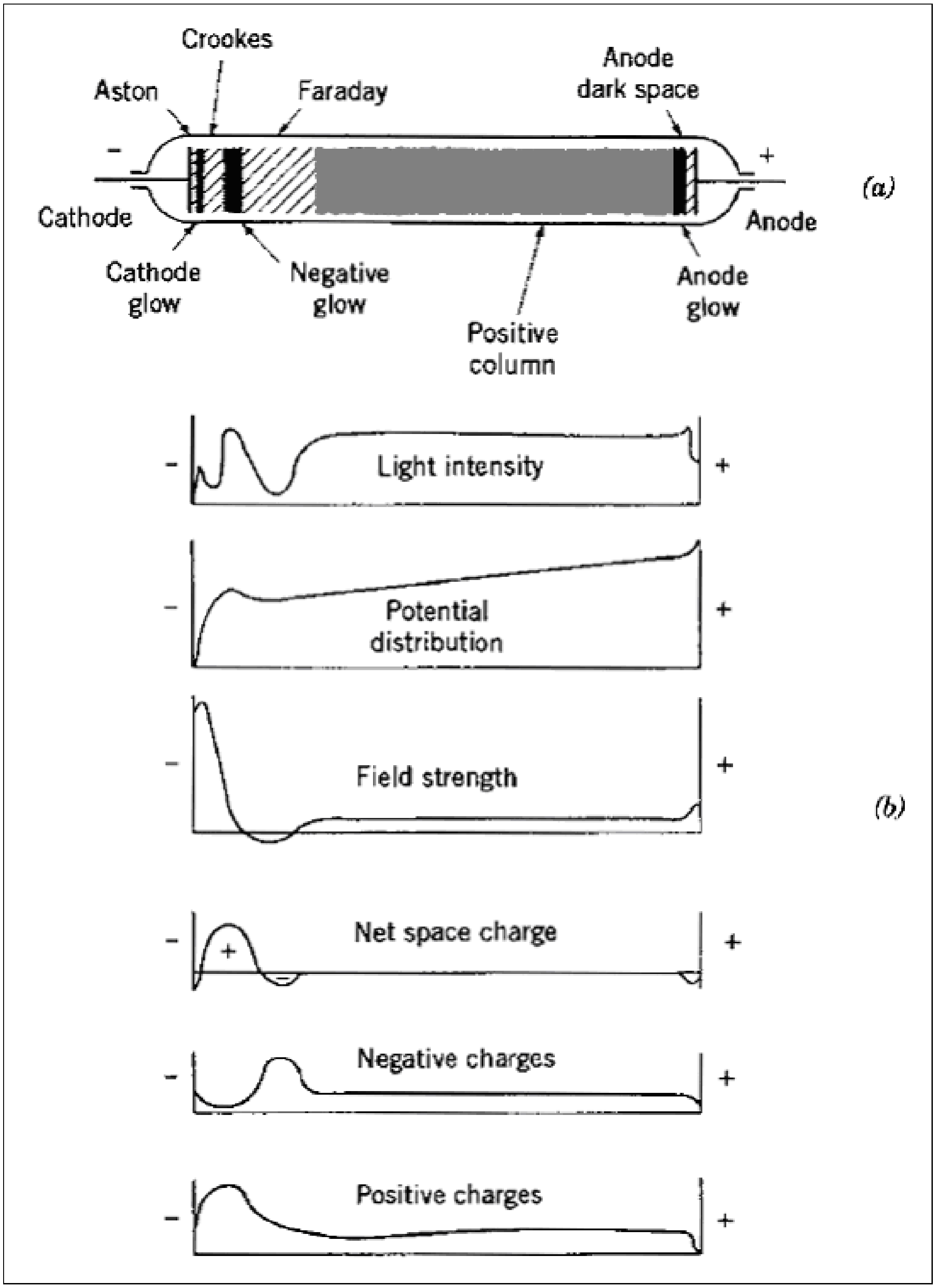


Figure 2.4: Typical characteristics of a normal glow discharge [10].

2.7 RF (Radio Frequency) Discharges

RF glow discharge and DC glow discharge plasmas are similar in many ways. The main difference is that RF glow discharge can be used to treat both conductors and non-conductors while DC glow discharge cannot [12].

The superiority RF glow discharge over DC glow discharge in their applications to material processing is due to several advantages namely wider range of operating parameters; more stable plasma; less affected by surface oxidation; greater sputtering depth [12].

In current practice, glow discharge processes used for the treatment of insulating materials are often driven by high frequency power source, usually in the megahertz (MHz) range. For an AC discharge, conventional main frequency (50 Hz) was found to be not very effective for the treatment of insulator. It is because if the time during which the insulator charge up is much less than half the period of the AC supply, then most of the time the discharge will be off. Thus at low frequency, there will be series of short-lived discharges with the electrodes successively taking opposite polarities [13].

When estimating the time to charge up the insulator by considering the voltage rise across the capacitor, although the current i to the target will actually decrease as the target charges up, it will be sufficient to regard it as constant. Therefore, the charge accumulated in t seconds will be $Q = it$ [13].

$$C = \frac{Q}{V} = \frac{it}{V} \quad , \qquad \text{(2.2)}$$

$$t = \frac{CV}{i} \quad . \qquad \text{(2.3)}$$

For example, the capacitance of a piece of quartz 1/8" thick is about 1 pF/cm^2, the applied voltage V is 1000 volts, the current density Q is 1 mA/cm^2, and assumed the RF ion currents are similar to DC sputtering currents, ~ 1 mA/cm^2 [13].

Therefore,

$$t = \frac{CV}{i} = \frac{1\times10^{-12}(1000)}{1\times10^{-3}} = 1\times10^{-6} \text{ s} \quad . \qquad \text{(2.4)}$$

This means a discharge can be produced continuously at frequencies above about 1 MHz (where frequency, $f = \frac{1}{t}$). In actual case, the insulator will not charge up so rapidly, because the current will not be sustained at a constant value. In practice, a discharge can be maintained quasi-continuously for frequencies above 100 kHz [13].

Many RF glow discharge processes operate at the frequency of 13.56 MHz. It is just because it is the frequency allocated by international communications authorities at which one can radiate a certain amount of energy without interferring with communications. However, RF glow discharge has so many nonlinear effects that it generates harmonic frequencies. Some of the harmonics falls in the VHF broadcast band and aircraft communication bands, etc. [13]. Therefore, operating frequencies are basically chosen at which it can optimize performance.

Typical values for the operating regime of capacitively coupled RF parallel plate reactors used for plasma processing are shown in Table 2.2 [8].

Table 2.2: Operating regime of capacitive plasma reactors used for plasma processing of insulating materials [8].

Parameter	**Low value**	**Typical value**	**High value**
Frequency	1 kHz	13.56 MHz	100 MHz
Gas pressure	3 mTorr	300 mTorr	5 Torr
Power level	50 W	$\approx$ 200 W	500 W
rms electrode voltage	100 V	$\approx$ 300 V	1000 V
Current density	0.1 mA/cm^2	$\approx$ 3 mA/cm^2	10 mA/cm^2
Electron temperature, T_e	3 eV	$\approx$ 5 eV	8 eV
Electron density, n_e	10^{15}/m^3	$\approx 5\times10^{15}$/m^3	3×10^{17}/m^3
Ion energy, ε_i	5 eV	50 eV	500 eV
Electrode separation, d	0.5 cm	4 cm	30 cm

2.8 Plasma Sheath

The plasma sheath is the most important region within a glow discharge. It is a thin positively charged layer formed in front of the surface of object placed inside the plasma. Consider a plasma with $n_e = n_i$ initially confined between two grounded ($\Phi = 0$) absorbing walls (Figure 2.5a). As the net charge density, $\rho = e(n_i - n_e)$ is zero, the electric potential, Φ is constant (or zero) and the electric field, E is zero in the entire plasma. Therefore, the fast-moving electrons are not confined, and will be lost rapidly to the walls. In a very short time, the lost of the electrons near the walls leads to the situation shown in Figure 2.5b. A thin positive ion sheath is formed near the wall in which $n_i >> n_e$. The net positive charge density within the sheaths leads to a potential profile that is positive within the plasma and falls sharply to zero near the walls [10]. The voltage across the sheath has influence on the energy of the ion striking the substrate. The ion enters the sheath with very low energy, then accelerated by the sheath voltage, and in the absence of collisions in the sheath, the ion would strike the substrate with a kinetic energy equivalent to the sheath voltage [13].

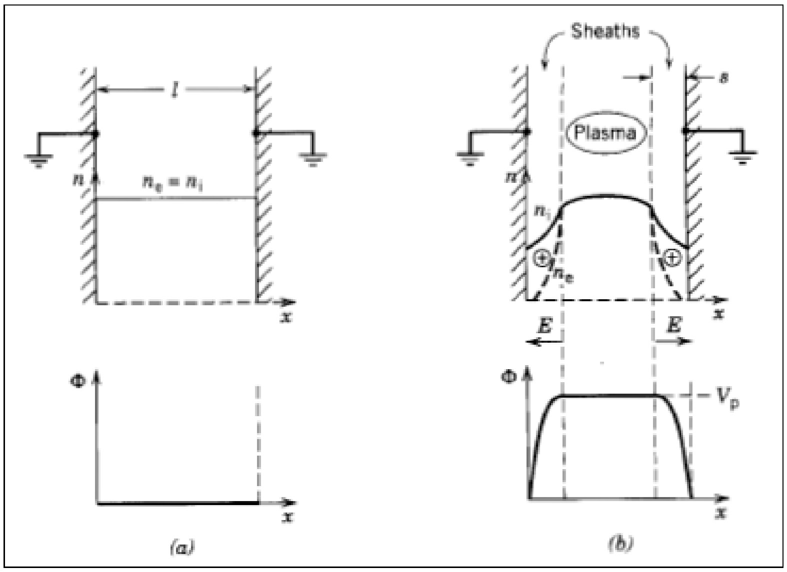


Figure 2.5: The formation of plasma sheaths: (a) initial ion and electron densities and potential; (b) densities, electric field, and potential after formation of the sheath [10].

In principle, the sheath thickness, *s* can be determined by solving the Poisson equation in the sheath region, using the sheath charge density, n_s. Assuming a uniform ion density in the sheath, $n_s = n_i$ = constant, and choose x = 0 at the grounded wall, we get [6]

$$\frac{d^2\Phi}{dx^2} = -\frac{en_i}{\varepsilon_0} \quad \text{.......(2.5)}$$

Set $\Phi(x = s) = V_p$, the matrix sheath thickness is

$$s = \left(\frac{2\varepsilon_0 V_p}{e n_i}\right)^{\frac{1}{2}} . \qquad \text{……………………………………………………………...(2.6)}$$

2.9 Energy Distribution Function

The velocities of particles in a plasma at thermal equilibrium are expected to follow the Maxwell distribution. The one-dimensional Maxwell distribution is given by

$$f(\upsilon_x) = A\exp\left(-\frac{m\upsilon_x^2}{2k_B T}\right), \qquad \text{……………………..……………………………(2.7)}$$

where $fd\upsilon_x$ is the number of particles per cm^3 with velocity between υ_x and $\upsilon_x + d\upsilon_x$, $\frac{1}{2}m\upsilon_x^2$ is the kinetic energy, and k_B is Boltzmann's constant.

The density, n (number of particles per cm^3), is given by

$$n = \int_{-\infty}^{\infty} f(\upsilon_x)d\upsilon_x \ , \qquad \text{……………………………………………………….(2.8)}$$

and the constant A is related to the density, n by

$$A = n\left(\frac{m}{2\pi k_B T}\right)^{\frac{1}{2}} . \qquad \text{…………………………………………………………(2.9)}$$

Therefore,

$$f(\upsilon_x) = \frac{dn}{d\upsilon_x} = n\left(\frac{m}{2\pi k_B T}\right)^{\frac{1}{2}} \exp\left(-\frac{m\upsilon_x^2}{2k_B T}\right) . \qquad \text{……………………………….(2.10)}$$

In three dimensions, the relation between the three velocity components $(\upsilon_x, \upsilon_y, \upsilon_z)$ and the speed, υ is given by

$$\upsilon^2 = \upsilon_x^2 + \upsilon_y^2 + \upsilon_z^2 . \qquad \text{…………………………………………………………(2.11)}$$

The distribution function in 3-D is given by

$$f(\upsilon) = \frac{dn_\upsilon}{d\upsilon} = \frac{4n}{\pi^{1/2}}\left(\frac{m}{2k_B T}\right)^{\frac{3}{2}} \upsilon^2 \exp\left[-\frac{m\upsilon^2}{2k_B T}\right] . \qquad \text{………………..………….(2.12)}$$

The distribution functions for three kinetic temperatures, $T_1 < T_2 < T_3$ are shown in Figure 2.6. The distribution function spreads out to higher velocities as the kinetic temperature of the plasma is increased. The area under the curves remains constant as long as the plasma is confined to a fixed volume.

When expressed in terms of kinetic energy, $\varepsilon = \frac{1}{2}m\upsilon^2$, the Maxwellian energy distribution function is given by

$$f(\varepsilon) = A\exp\left[-\frac{\varepsilon}{k_B T}\right]. \qquad \text{…………………………………………………….(2.13)}$$

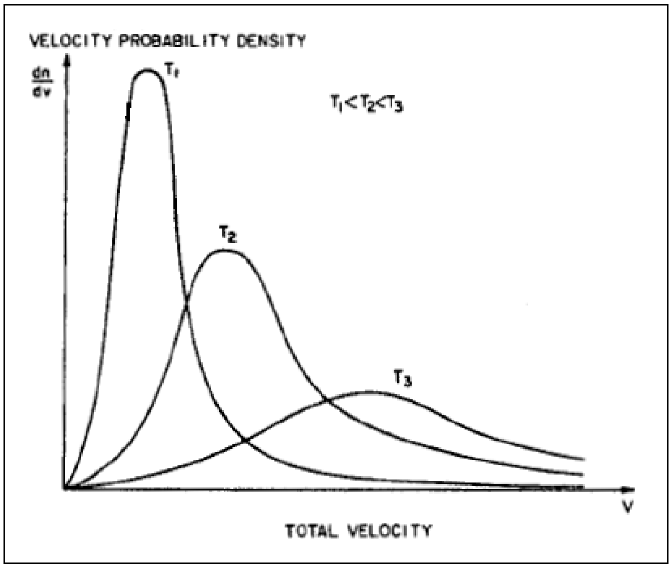


Figure 2.6: The distribution functions for three kinetic temperatures, $T_1 < T_2 < T_3$ **[8].**

In the actual situation, the electrons in the glow discharge may not have achieved a total thermal equilibrium. The slower electrons make elastic collisions while electrons with energies above the excitation and ionization thresholds are making inelastic collisions, and lose a large fraction of their energy. Besides, fast electrons are also lost rapidly by diffusion to the walls and recombination. Therefore, there is a shift of electrons from high energy to low energy states, and it might be expected to have fewer electrons with high energies than predicted by Maxwell distribution [10].

Although the Maxwell statistics describes the thermal equilibrium state, where the motion of the particles of the system is perfectly random, the distribution function is also often used in near thermal equilibrium situations. The reasons for this are: (1) the system may only be slightly deviated from thermal equilibrium, and (2) the actually distribution function of the system may be very difficult to determine. The Maxwell distribution function may be used as a valid first approximation and it can be mathematically manipulated with relative ease [14].

The Druyvesteyn distribution is supposed to be more realistic as in this case the motion of electrons in a weak electric field is being considered. It predicts more electrons with energies around the average energy and fewer high energy electrons in a system as compare to the Maxwell distribution. However, the inelastic collisions are still ignored. Druyvesteyn distribution function falls off more rapidly at high electron kinetic energies, and it is characterized by a considerably steeper decrease of the number of electrons in the high energy tail than that of the Maxwell distribution, as shown in Figure 2.7 [10, 13].

The Druyvesteyn distribution function is given by [13]

$$f(\varepsilon) = A\exp\left[-\frac{3m}{M}\frac{\varepsilon^2}{\varepsilon_0^2}\right] \quad ; \quad \varepsilon_0 = eEl \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.14)$$

where

m = electron mass

M = ion mass

e = electron charge

E = electric field

$l = \frac{\upsilon}{\nu_m}$ = free path length of electrons (ν_m = effective collision frequency)

ε_0 = energy gained by an electron from the field over a free path length

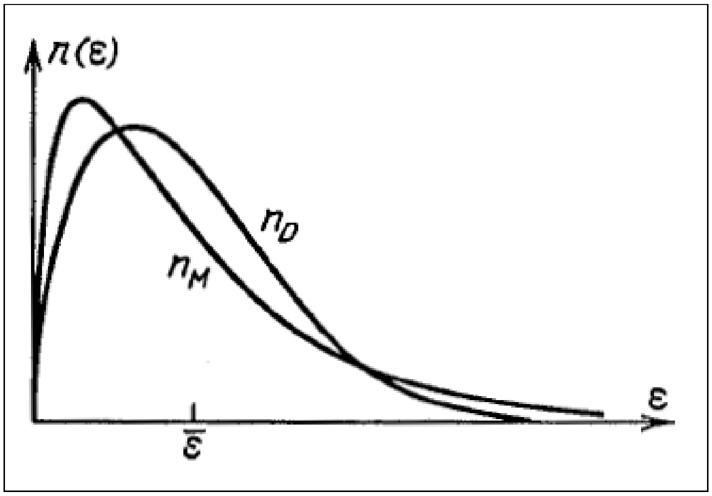


Figure 2.7: Maxwellian (n_M) and Druyvesteyn (n_D) distribution function in energy, n(ε) [13].