

### 10.3.1.5 Low pressure electrical discharges (LPED)

*Low pressure electrical discharge* (LPED) sources are radiation sources in which radiation is produced by electrical discharges in gases at low pressures, i.e., pressures from  $10^{-2}$  to  $10^3$  Pa. (*Source* is the preferred term when a low pressure electrical discharge is used as the sampling source. The term *lamp* usually indicates a primary source that is permanently sealed). Atoms or molecules of the samples to be analyzed are present or are introduced into the discharge. Usually one of the *noble gases*, such as argon or neon, is used, but mixtures of these gases and/or small quantities of *diatomic* or *polyatomic gases* may also sustain a discharge. Such a gas is called the *carrier gas*. The carrier gas is the main gas responsible for the conductance of the electrical current.

Generally, the sample is introduced by making it form a part of the cathode and, as a result of *ionic bombardment* and *atomic bombardment* of its surface, material is removed by the process of *cathodic sputtering* and/or thermal evaporation. This material enters the plasma and atoms are excited to produce characteristic radiation. If the sample is already in a gaseous form, it may be introduced into the discharge separately or mixed with the carrier gas.

The processes of LPED are explained in terms of a classical discharge chamber of cylindrical shape in which two plane electrodes of conductive materials are separated by a distance  $l$  (see Fig. 10.4). The pressure, voltage and current are three controllable and variable parameters which may be interdependent.

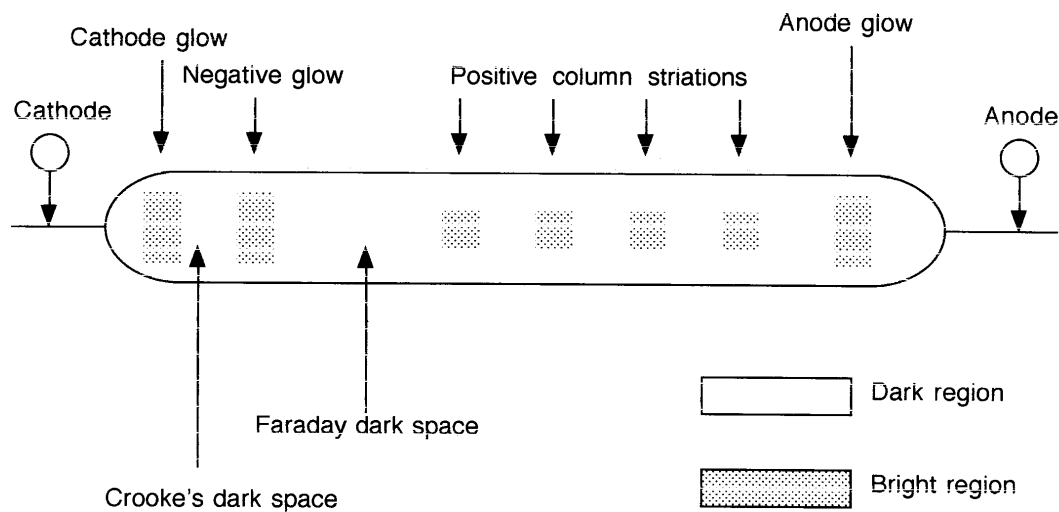


Fig. 10.4 Schematic Diagram of a low pressure electrical discharge between plane electrodes

The vessel may be sealed or it may be flushed (pumped) continuously with carrier gas. In such sources the flow is controlled either by means of a *needle valve* or a *gas-restricting orifice*.

#### 10.3.1.5.1 Radiation

If the vessel is evacuated to high vacuum, the carrier gas allowed to fill it to a predetermined low pressure and a voltage applied to the electrodes from a dc source, a current will flow. This current will initially be very small, but once the voltage reaches the *breakdown voltage*,  $U_{br}$ , a higher current will flow between the anode and cathode, depending on the characteristics of the external circuit.

Simultaneously with the flow of current, a *glow discharge* with specific characteristics will develop between the electrodes as shown in Fig. 10.4 which also illustrates the *spatial distribution of radiation* from the cathode to the anode with its specific luminous characteristics.

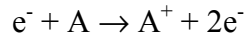
At the cathode a narrow dark space (*Aston dark space*) is seen. A slightly luminous layer then occurs. This is called the *cathode glow*. Then a non-luminous volume known as the *cathode dark space* (or *Crookes [Hittorf] dark space*) is seen, which has a sharp boundary with the highly luminous *negative glow*. The negative glow tails off into the *Faraday dark space*, followed by another luminous region. This luminous region, called the *positive column*, may have several alternating or moving dark and luminous regions. Should the positive column have structure, these luminous and dark regions are called *striations*. Near the anode, another dark space occurs (the *anode dark space*). The anode itself is usually covered with a slightly luminous sheath called the *anode glow*. If the distance,  $l$ , is changed while maintaining constant pressure and voltage, the axial lengths of the zones from the cathode to the positive column remain unaltered. The length of the positive column will change, however. If the anode is brought so close to the cathode that it enters the negative glow, the positive column may disappear completely, but all other parameters of the discharge remain almost the same.

The dimensions of the *negative zones* are dependent on the pressure, on the shape and area of the cathode and on the current.

#### 10.3.1.5.2 The discharge

At a voltage less than the breakdown voltage, *residual ionization*, which is present in any gas (this ionization may be caused by interatomic collisions or by charged particles due to the presence of *cosmic radiation*), results in a *dark* (non-luminous) *discharge*. At the breakdown voltage electrons are released from the cathode at their *ejection energy* ( $\sim 1$  eV). Because of this low energy, these electrons are unable to transfer their energy on collision to the excitation of atoms (Aston dark space). As they are accelerated through the *cathode fall region*, the region of high potential gradient, they gain enough energy to

excite atoms by collision. This results in the luminous *cathode glow*. Other electrons acquire energies in excess of the excitation energy and are rapidly accelerated into the cathode (Crookes) dark space. Here they collide with neutral atoms of the carrier gas causing ionization.



*Electron multiplication* occurs, but the electron population consists of two distinct groups - fast and slow electrons. Fast electrons are those initiated at or near the cathode, and slow electrons are those created by ionization processes.

Slow electrons are only partially accelerated by the cathode fall potential and have a current-energy distribution sufficient to cause excitation of gas atoms in the highly luminous negative glow.

Fast electrons finally impart their energy through collisions of the first kind to cause ionization. Due to the weak potential gradient in the positive column, they are then unable to achieve significant energy.

Partial acceleration and loss of energy through excitation, which may take place repeatedly, cause the striations in the positive column.

A *Penning gas mixture* consists of a rare gas containing impurity atoms, often at very low concentrations. The impurity atoms have an ionization potential  $V_{\text{ion}}$  which is lower or equal to the metastable potential ( $V_{\text{meta}}$ ) of the parent noble gas.

The *Penning effect* in a Penning gas mixture is the ionization by *charge transfer (charge exchange)* during collision between a metastable atom and a neutral atom which decreases the average energy to form an ion pair, e.g.,  $\text{Cu} + \text{Ar}_{\text{meta}} \rightarrow \text{Cu}^{+} + \text{Ar} + e^{-}$ . In a glow discharge, this results in an increase of the *ionization coefficient (Townsend first coefficient)*, a decrease in breakdown potential and a lowering of the cathode fall potential.

The *magnetic Penning effect* describes the increase of the *ionization probability* of gas in a low pressure electrical discharge resulting from the helical (spiral) movement of electrons in a magnetic field placed normal to the anode-cathode electrical field.

#### 10.3.1.5.3 Cathodic sputtering

Ions from the Crookes dark space are accelerated towards the cathode. Most of the positive ions impinge upon the cathode and by *momentum transfer* impart their energy in a succession of *binary collisions* to atoms in a surface layer of the cathodic material. Other ions in their movement towards the cathode become neutralized, either by *free electrons* in the *space charge* near the cathode or by charge transfer with other atoms, but still maintain their momentum towards the cathode. (The process of deionization is also

described as *electron capture*. Atoms created in this way carry no charge and are thus unaffected by space charges). A large portion of these atoms will impart their energy to the cathode. Some ions enter the *crystal lattice* by a process called *channelling*, releasing their energies within the crystal. Part of the energy released below the surface is transported to the topmost monolayer by way of *collisional chains* and gives rise to the ejection of atoms from the sites where the collision chains terminate. Ejected atoms include atoms of gases absorbed on to the surface of the cathode.

The process is called *cathodic sputtering* and is characterised by the *sputtering yield*,  $S_{sp}$ , the number of sputtered atoms released per incident ion and the *sputtering rate*,  $q_{sp}$ , the amount of material sputtered per unit time. *Clean up* is a process caused by sputtering, *trapping* (or adsorbing) metallic atoms, gas atoms or molecules on the walls of the vessel or anode. This has the effect of reducing the gas pressure in sealed lamps, and may be useful for cleaning up or *gettering* unwanted gases.

#### 10.3.1.5.4 Types of glow discharge

If the discharge vessel shown in Fig. 10.4 and referred to in this section is kept at a constant pressure of about 100 Pa and the applied voltage increased while the current is measured, the voltage-current relationship enables discharges with specific discharge characteristics to be identified.

The *normal glow discharge* is characterized by a constant burning voltage,  $U_b$ , for a range of current from  $\sim 10^{-5}$  -  $\sim 10^{-2}$  A. The current density at any point at the cathode remains constant, but the cathode area is not fully covered by the glow. The onset of the normal discharge is highly dependent on the shape, size and the material of the electrodes, the carrier gas and the impurity gases and, to a lesser extent, on the shape of the containing vessel. As the current increases, more of the cathode becomes covered by the glow.

After the negative glow fully covers the cathode area, a further increase of current results in a rise in the burning voltage and thus in the current density. This is the *abnormal glow discharge*. The voltage and current rise almost linearly for a current range of  $\sim 5 \times 10^{-3}$  -  $10^{-1}$  A. After this current is reached, the ion bombardment on the cathode is so energetic that thermal effects cause the discharge to change to an electric arc.

An abnormal glow discharge also results when the area of the cathode in the original normal discharge is reduced. This is called a *restricted glow discharge* or a *restricted abnormal glow discharge*. This occurs, for example, when an *annular anode* that restricts the cathode area is placed within the cathode fall region of the discharge. *Differential pumping* of the gap to a higher vacuum than the discharge region enlarges the cathode fall in that region. The restricted [abnormal] discharge should not be confused with the *constricted glow discharge*. In the constricted discharge, the radius of the vessel between the anode and cathode is reduced to the order of one *free ionic path length*. Fast

electrons from the cathode reach the anode and produce X-rays which, together with fast positive ions, release secondary electrons from the cathode.

The *spray discharge* develops when a very thin insulator or *semi-conducting surface*, (e.g., an oxide layer) covers the cathode. A discharge without a dark space develops. The cathode fall is lower and a much higher voltage is required to sustain the discharge.

#### 10.3.1.5.5 Arc lamps

Certain spectral radiation sources in sealed vessels operate as arcs at low pressures. They are known as *arc lamps*. These arcs are sustained mainly as a result of thermal processes and are characterized by a cathode fall potential much lower than a glow discharge, a thinner cathode glow region and high current densities. The spectrum emitted is due to the discharge gas and the cathode material. Atomic line spectra are dominated by transitions of the lower energy levels of neutral atoms.

*Low pressure arc lamps* ( $10^2 - 10^5$  Pa) may have supplementary heating of the electrodes to strike (*initiate*) the arc and constricting devices to increase the *positive column current density*, resulting in increased *spectral radiance*. Low pressure arcs usually require voltages between 300 and 600 V to strike, but the operating voltage falls once the arc is initiated.

*Metal vapour arc lamps* usually contain metals with low melting points and low ionization potentials. These include the alkali metals, some alkaline earths and metals such as mercury and cadmium. Mercury, having a high vapour pressure, does not usually require supplementary heating of electrodes.

*High pressure arc lamps* ( $>100$  kPa) give broadened spectral lines, but have high intensities and heavy continuous backgrounds. Low pressure arc lamps give lower intensities, but have narrower spectral lines.

Metal vapour lamps usually operate on alternating current so that anode and cathode construction can be identical. Argon and neon are the most commonly used carrier gases. Arc lamps are used as primary spectral radiation sources, e.g., for atomic absorption spectroscopy, calibration of spectrometers and spectrographs and for lighting purposes.

#### 10.3.1.5.6 Geissler Lamps

*Geissler lamps* are glow-discharge sources operating in the normal mode. They have a *capillary tube* between the annular anode and cathode to constrict the discharge of the positive column. These sources are either continually flushed or sealed. The excitation mechanism of Geissler sources involve atoms being excited in the positive column. Constriction results in the availability of fast electrons to cause ionization of the carrier gas.

The main usage of these sources is for gas analysis. Impurity gases are bled into the vacuum system. Spectra are viewed end-on through the annular anode. Molecular spectra may also be measured if the capillary tube between the electrodes is not too narrow.

#### *10.3.1.5.7 Hollow cathode sources*

The *hollow cathode sources* (*hollow cathode lamp* [HCL]) have cylindrically shaped cathodes, one end of which may be closed. In a normal hollow cathode, the ratio of length to diameter is  $>1$ . *Open-ended hollow cathodes* have both ends open. The *hollow cathode discharge* may operate as an abnormal or a normal discharge, depending on the dimensions of the cathode, the carrier gas and the cathode material. Complex ion, electron and photon processes take place in the discharge and give rise to profuse cathodic sputtering and high spectral line intensities. When used as sampling sources, they are usually continually flushed to remove impurity gases generated from the sample in the cathode.

In the *cold hollow cathode source*, the cathode is cooled externally (e.g. by air, water or liquid nitrogen).

*Hot hollow cathode sources* are designed to enable the temperature of the cathode to rise appreciably and to cause material to be vapourized by thermal heating as well as by sputtering. The temperature may be so high that the material in or on the cathode is liquid or molten. This material may be a sample introduced into the cathode.

*Sealed hollow cathode lamps* are used as primary sources for atomic absorption spectroscopy because of their relatively intense radiation, narrow spectral lines and stable emission (when operated from current-stabilized supplies).

*High intensity hollow cathodes* are made by shielding the cathode lip or reducing its diameter, and thus increasing the current and ion densities. This partly inhibits the emission of sputtered material and may result in a higher atomic line intensity per unit current. The terms high brightness or hi-brightness are not recommended.

With *boosted hollow cathode sources* it is possible to increase the intensity of the *primary discharge* by introducing a *secondary discharge* via one or two *supplementary electrodes*. The electrodes may be placed so that the *supplementary discharge* (mainly its positive column) runs across the front of the cathode or through an open-ended cathode. The supplementary electrodes are made from or are coated with material having a low work function, so as to enable the supplementary discharge to be of lower voltage than the primary (glow) discharge. They may also be resistively heated. Supplementary discharges are generally aimed at enhancing the resonance spectral lines to obtain higher

intensities with reduced self-absorption effects. *Intensity modulated hollow cathode lamps* are widely used in atomic absorption and atomic fluorescence spectroscopy.

Hollow cathode sources are used as sampling sources for the emission analysis of small quantities of materials or where material should not be lost, e.g., precious metals (gold) or radioactive materials. Elements with high excitation potentials may be excited in a hollow cathode discharge to give stable and narrow line spectra.

They have been used as high resolution sources, e.g., for *isotopic analysis*, vacuum ultraviolet studies, gas analysis and the analysis of non-metals. They are also well suited as sample sources for gas analysis.

#### 10.3.1.5.8 Plane cathode glow-discharge sources

*Plane cathode glow-discharge sources* (e.g., *Grimm glow-discharge source*) operate under abnormal glow-discharge conditions. The sample, which must have a plane surface, is made the cathode of the discharge. Restriction of the area to be sputtered can be achieved by several means, e.g., by using an annular anode which faces the sample surface with such a small gap (100-200  $\mu\text{m}$ ), that no *short circuit discharge* can occur. Another device for restricting the discharge is a *restrictor plate* made from an insulating material and placed close to the cathode.

The discharge is essentially abnormal and voltages of up to 2 kV may be used. The gas flow flushes away *residual* or absorbed *gases* released from the cathode. The high operating voltages enable profuse sputtering to take place, even from poorly conductive materials. The flow of gas across the sample surface is radially away from the surface so that atomic species, including gas released from the sample, are swept away. This results in an *optically thin plasma* with little self-absorption of lines.

It is possible to introduce supplementary electrodes to provide a secondary discharge and, by so doing, to enhance the sample spectra. This discharge may be modulated and, by using a *tuned amplifier measuring system*, only the enhanced radiation is measured. This lamp is called a *boosted output glow-discharge source*.

Glow discharges may be operated under the influence of an external magnetic field. Such *magnetic field glow-discharge sources* have either a permanent magnet or an electromagnet to achieve enhanced intensities and more profuse sputtering. If, in such a discharge source, one or more supplementary electrodes are introduced to modify the discharge, it is called a *boosted magnetic field glow discharge source*.