Chapter 2

Development of a tetrode type electron gun for generation of low energy electrons and its use for the synthesis of nanoparticles in PVA matrix

A tetrode type electron gun system for the generation of low energy electrons was designed, developed and characterized. An electron gun having four electrodes namely cathode, focusing electrode, control electrode and anode has been designed for the irradiation experiments. This electron gun is capable to provide electrons of energy over the range of 1 keV to 20 keV, with current maximum upto 100 µA. This system is being used for the synthesis and diffusion of metal and semiconductor nanoparticles in polymeric materials. Using this method, gold nanoparticles have been synthesized by irradiating gold coated PVA (Polyvinyl Alcohol) sheets. The electron fluence was varied from coating to coating upto $24 \times 10^{15}$ e/cm$^2$. The irradiated samples were characterized by the UV–Vis, XRD, SEM and RBS techniques. This method of synthesis of metal nanoparticles by low energy electron beam irradiation has the key importance in the development of new fabrication techniques for nanomaterials.
PART A: Development of a tetrode type electron gun for low energy electron irradiation system

2.1 Introduction

Development of electron sources has gained unique importance in the areas of fundamental research as well as for their use in various applications [1]–[6]. The different parameters of an electron beam such as energy, current, spot size, beam uniformity, etc are decided by the requirements [7], [8]. In any electron gun system, the geometry of the electrodes decide the main beam optics comprising of uniform flow of electrons, beam waist, focusing and defocusing and the axial location of the beam spot [9]–[13]. Electron gun systems delivering electrons of range of energies have been developed according to specific uses [14]–[16]. Low energy electron sources find applications in fundamental research as well. Using low energy electrons, a number of investigations [17] are being carried out in several areas such as irradiation effects on the surface properties of semiconductors, charge dynamics in electron irradiated polymers, charge storage property of insulators, X-ray generation, discharge characteristics of the spacecraft materials etc. [18]–[20].

2.2 Review of electron guns designed by different workers

In literature one can find various designs of different types of electron guns and their modifications for better output. S. K. Mahapatra [17] has reviewed all the important electron guns designed and developed by various researchers. Pioneer researcher J. R. Pierce [21] discussed how the shape of the electrodes can affect the rectilinear flow of electron beam. Smith and Hartman [22] proposed the concept of potential variation dependence of a function of $d^{4/3}$ where, $d$ is the distance along the axis of an electrode system. The main focus of this study was to obtain rectilinear flow of the electrons. Along with the rectilinear flow of the electrons, attempts have also been made for the radial flow of the electrons. In this respect, the work of Langmuir and Blodgett is important for researchers working in the field. The equipotential lines of concentric cylinders are made use of for the radial flow of electrons [23], [24]. The Vaughan method [25] is explicitly reported on the design of pierce type electron guns. In a paper published 1999, Tiwari and Basu [27] proposed
a method to design the half beam cone angle and then used the similar formulations for the design of all the other parameters. However, they did not discuss about the design of anode aperture. A Steigerwald type electron gun [26], [27], proposed by Steigerwald in 1949, which was a simple triode system with a modified Wehnelt grid which causes tele focusing. This electron gun design is known for generating a very narrow and well collimated beam used for high energy electron scattering experiments. The emission characteristics of the steigerwald type electron gun have first investigated in a systematic way by Braucks in 1958 [28]. Other various types of electron guns have been designed and developed by different researchers for specific applications. These electron guns were developed by Manfred Flink et al. [29], V. P. Ovsyannikov et al. [30] and B. Schiewe et al. [12] etc. These electron guns provide focused beam with diameter in the range of µm to a few mm. Such types of electron gun systems are not suitable for synthesis of nanomaterial in polymer matrix or any other medium in which the sample area may vary from $10^2$ to $10^4$ mm$^2$.

For a small beam getting incident on the sample, the beam cannot cover the entire sample surface area. In such case, the electron beam is scanned for covering the entire sample area of the sample. However, this type of experiment has a drawback that the distributions of the electron dose remain uneven over the sample. It is therefore desirable to have a system in which the spot size of the electron beam can be varied for a wide range so as to cover the entire sample area. From last decade, the low energy electron sources have gained importance because of the requirements of simulating conditions of the space environment [8], [31], [32]. With advent of technology, the electron emitting materials and advance methods of computation of electrostatic and magnetic lines of forces, any design of electrodes in the electron gun can be achieved. For many experiment, it is desirable to have an electron source with beam size.

2.3 Theory of electron gun

2.3.1 Electronic emission

In the thermionic electron gun, electrons are emitted from filament (tungsten based materials) and then accelerated towards the anode by applying a potential difference across the electrodes. The functioning of the electron gun depends on the work function of the filament, its shape and configuration of the electrodes. The
stability of the electron beam depends on the material of the filament used in the electron gun.

The electrons are emitted from the conducting filament by thermal heating, where outer orbital electrons gain sufficient energy to overcome the work function barrier of the conductor. This type of emission is called thermionic emission. The energy required for the material to give up electrons is related to its work function \( E_w \) as, \( E = E_w + E_f \). Here, \( E \) is the total amount of energy needed to remove an electron to infinity from the lowest free energy state, \( E_f \) is the highest free energy state of an electron in the material and \( E_W \) is the work function or work required to achieve the difference. Electrons travel away from the cathode with an average energy of \( E = kT \), where \( k \) is Boltzmann's constant and \( T \) is the filament temperature (K). In order to flight from the filament, electrons must have a velocity component at right angles to the surface and their corresponding kinetic energy must be at least equal to the work done in passing through the surface [17].

The current density emitted by a hot heated filament is expressed by the equation,

\[
j = AT^2 e^{-\frac{E_W}{kT}}
\]

Where,

- \( j \) = the current density \(( \text{A cm}^{-2} )\),
- \( A \) = Richardson-Dushman constant \((37 \text{ Acm}^{-2} \text{ K}^2)\),
- \( T \) = the temperature in Kelvin,
- \( E_W \) = the work function and \( k \) is Boltzmann’s constant.

To maintain the electron current at a set value it is necessary to maintain the temperature of the filament at a constant value. The current is also depending on the work function. For high currents, the \( E_W \) must be kept low[17].

### 2.3.2 Design of the electrode

As mentioned earlier, the electrons are emitted from a hot filament, mounted on cathode. These electrons are accelerated across the space between cathode to anode by applying potential such that electrons get accelerated towards anode. At high current density, a space charge can be built up. This space charge has ability to deform the equipotential lines across the cathode and anode. An uncompensated space charge repulsive force gets originated and the electron beam
shows a tendency to spread out as it traverses from cathode to anode. However, it is possible to obtain a rectilinear flow by supplying compensating forces along the beam edge. Theoretical background considered while designing the electrode is explained in detail in the thesis of S. K. Mahapatra [17].

While studying the basic design, the following assumptions have been considered:

1. The magnetic field effect due to the traversing electrons is neglected
2. The thermal velocities of the traversing electrons are neglected
3. Only electrostatic forces are considered

Under these assumptions, the electron velocity \( v_e \) at any point is specified by a potential \( \phi \) and at \( \phi=0; \ v_e = 0 \). The charge density \( j_0/v_e \) is continuous; where \( j_0 \) is the current density which is constant throughout the flow and \( v_e \) is the electron velocity as specified by \( \phi \).

The governing Poisson’ equation for the region between the electrodes of the electron gun is written as

\[
\frac{d^2 \phi}{dx^2} = \frac{Ze \cdot n(x)}{\varepsilon_0}
\]  

(2.2)

In steady state, current density, \( j_0=Ze \cdot n(x) \cdot v_e(x) \), is the same at all positions in the gap. The particle density as a function of position is given as

\[
n(x) = \frac{j_0}{Ze \cdot v_e(x)}
\]  

(2.3)

Whereas, if considering the electrostatic potential to be zero at the particle source, the particle velocity is expressed as

\[
\frac{m_0 v_x^2}{2} = Ze \phi
\]  

(2.4)

Rearranging (2.3) and (2.4) and substituting in (2.2) the one-dimensional Poisson equation (2.2) can be rewritten as

\[
\frac{d^2 \phi}{dx^2} = \frac{-j_0}{\varepsilon_0 \cdot \sqrt{2 \cdot Ze \cdot \phi/m_0}}
\]  

(2.5)

Eq. (2.2) is thereby solved with appropriate boundary conditions so as to find the self-consistent variation of \( \phi(x) \). Substitution of \( \phi(x) \) in Eq. (2.3) gives the
variation of particle density. The steps in the self-consistent equilibrium calculation for this special case are as follows.

Firstly, conservation of energy and particle flux is used to express the beam density as a function of the field quantity, $\phi$.

Secondly, substitution of the expression into the field equation to find $\phi$. Eq. (2.5) can be more efficiently rewritten by introducing the dimensionless variables $\xi = x/d$, $\Phi = -\phi/V_o$. Eq. (2.5) takes the form as

$$\frac{d^2 \Phi}{d\xi^2} = \frac{\beta}{\sqrt{\Phi}}$$

(2.6)

where,

$$\beta = \frac{j_0 \cdot d^2}{\varepsilon_o \cdot V_o \cdot \sqrt{\frac{2 \cdot Ze \cdot V_o}{m_o}}}$$

(2.7)

Eq. (2.6) is solved by multiplying both sides by $2\Phi'$, where $\Phi' = d\Phi/d\xi$:

$$2 \cdot \Phi' \cdot \Phi'' = \frac{2 \cdot \beta \cdot \Phi^i}{\sqrt{\Phi}}$$

(2.8)

The left-hand side is an exact differential of $(\Phi')^2$. Eq. (2.8) is then integrated both sides for the regime, $x=0$; (the source position), to $x=x$; position. Appropriate boundary conditions have been applied.

$$[\Phi'(\xi)]^2 = 4 \cdot \beta \cdot \sqrt{\Phi(\xi)}$$

(2.9)

Eq (2.9) is rewritten as

$$\frac{d\Phi}{\Phi^{3/4}} = \sqrt{4 \cdot \beta} \cdot d\xi$$

(2.10)

Integrating both sides of Eq 2.9, it appears as

$$\Phi^{3/4} = \left(\frac{3}{4}\right) \cdot \sqrt{4 \cdot \beta} \cdot \xi$$

(2.11)

At the boundary condition $\Phi=1$ implies $\beta = 4/9$. Substituting $\beta$ from Eq. (2.7) and solving for the current density ($j_0$); the space charge is calculated from the well known Child law for space charge limited extraction:

$$j_0 = \frac{4 \cdot \varepsilon_0 \cdot \sqrt{\frac{2 \cdot Ze \cdot V_o^{3/2}}{m_0 \cdot d^2}}}{9}$$

(2.12)
The value of $V_0$ is obtained as

$$V_0 = \left[ \frac{9 \cdot j_0 \cdot \sqrt{m_0}}{4 \cdot \varepsilon_0 \cdot \sqrt{2 \cdot Ze}} \right]^{2/3} \cdot d^{4/3} \quad (2.13)$$

For space-charge-limited flow, the variation of electrostatic potential with position is given as

$$\phi(x) = V_0 \cdot \left( \frac{x}{d} \right)^{3/4} \quad (2.14)$$

where $V_0$ is applied voltage, $d$ is gap between cathode to anode and $x$ is the variable position between cathode and anode.

Substituting $V_0$ from Eq (2.13) into (2.14), the ultimate expression of the space charge potential distribution is written as

$$\phi(x,0) = \left[ - \frac{9 \cdot j_0 \cdot \sqrt{m_0}}{4 \cdot \varepsilon_0 \cdot \sqrt{2 \cdot Ze}} \right]^{2/3} \cdot x^{4/3} \quad (2.15)$$

Pierce has shown that the potential distribution as given by

$$\phi(x, y) = \left[ - \frac{9 \cdot j_0 \cdot \sqrt{m_0}}{4 \cdot \varepsilon_0 \cdot \sqrt{2 \cdot Ze}} \right]^{2/3} \cdot \text{Re}(x + jy)^{4/3} \quad (2.16)$$

It satisfies the Laplace equation $\nabla^2 \phi = 0$, outside the beam. Reducing the equation (A) at $y = 0$, zero electric field or zero potential gradient is obtained normal to the beam edge. It implies that $\partial \phi / \partial y = 0$ at $y = 0$.

According to Equation (2.16), equipotential surfaces are observed to be those for which $\theta = \tan^{-1}(y/x)$

$$\left( x^2 + y^2 \right)^{\frac{4}{3}} \cdot \cos \left( \frac{4}{3} \cdot \theta \right) = \left[ \frac{9 \cdot j \cdot \sqrt{m}}{4 \cdot \varepsilon_0 \cdot \sqrt{2 \cdot Ze}} \right]^{2/3} \quad (2.17)$$

The zero potential $V = 0$ is a plane, whose intersection with y-x plane is given by $y = x \tan 67.5$. The angle of 67.5 (or $\frac{3}{4} \times 90^\circ$) arises from the exponent 4/3 in equation (2.15) and is called as Pierce angle.
The converging or diverging electron flow between the electrodes in an electron gun is shown in figure 2.1. The cathode and anode are the spherical segments referenced to the same center. They have radii of curvature $r_c$ and $r_a$. A set of electrodes are placed outside the beam volume to produce a potential variation along the beam envelope that approximates the spherical flow solution. Trial-and-error calculations using numerical techniques are used to find the electrode shapes.

The perveance of a full spherical electron beam is given by

$$I_{sphere} = \frac{4e_0}{V_0^{3/2}} \frac{2e}{9} \sqrt{\frac{4\pi}{m_e}} \left[ \alpha \left( \frac{\rho_a}{\rho_c} \right) \right]^2$$

(2.18)

where $I_{sphere}$ is the total current from spherical cathode, $e$ is the electronic charge, the quantity $\alpha (\rho_a/\rho_c)$ is the Langmuir function ($\alpha = \gamma - 0.3 \gamma^2 + 0.075 \gamma^3 - 0.0143182 \gamma^4 + 0.0021609 \gamma^5 - 0.00026791 \gamma^6 + \ldots$, where $\gamma$ is $\ln (\rho_a/\rho_c)$) for converging flow. It depends on the radii of curvature of the cathode and anode.

The perveance of the electron gun equals the expression of Eq. (2.18) for complete spherical cathode. Here, the cathode area, $A_c$ to the area of a full sphere, $4\pi \rho_c^2$. The perveance for a unit area of cathode is given as

$$\frac{I}{V_0^{3/2}} = \frac{4e_0}{9} \frac{2e}{m_e} \sqrt{\frac{4\pi}{\alpha \left( \frac{\rho_a}{\rho_c} \right)^2}} \frac{1}{4\pi \rho_c^2}$$

(2.19)

In terms of the coordinate system, a differential surface element of the cathode is written as

$$dA_c = 2\pi \rho_c^2 \sin \theta \, d\theta$$

(2.20)
Integrating Eq. (2.20) from 0 to \( \theta \) gives

\[
A_c = 4\pi \rho_c^2 \left( 1 - \cos \frac{\theta}{2} \right) = 4\pi \rho_c^2 \sin^2 \left( \frac{\theta}{2} \right)
\]

(2.21)

For the area \( A_c \) of the cathode, the gun perveance as obtained from equation (2.19) is given as

\[
\frac{I}{V_0^{\frac{1}{2}}} = \frac{4\varepsilon_0}{9} \frac{2e}{m} \sin^3 \left( \frac{\theta}{2} \right) \left[ \frac{\rho_a}{\rho_c} \right]^3
\]

(2.22)

In practical units for electrons, Eq. (2.22) becomes

\[
P = 29.4 \sin^2 \left( \frac{\theta}{2} \right) \left[ \frac{\rho_a}{\rho_c} \right]^2
\]

(2.23)

Where, \( P = \left( \frac{I}{V^{\frac{1}{2}}} \right) \) is perveance of the electron gun in \( \mu \text{perv} \), \( \rho_a \) is the radius of curvature of anode and \( \rho_c \) is the radius of the curvature of the cathode. The electron gun consists of cathode (K), the focusing electrode (F), the control electrode (C) and the anode electrode (A). From gun design point of view, the geometry of this four electrode electron gun determines the perveance of the gun. Hence the required value of the perveance determines the choice of the shape of the electrodes in the electron gun.

### 2.4 The present electron gun (Simulation)

The present electron gun provides electrons of different energy upto 20 keV which can be used to study irradiation effects of these electrons on materials and synthesis of nanomaterials in the polymer matrix. Over this energy the perveance of the electron gun can reach upto 0.4 \( \mu \text{perv} \) [17]. Here, we have considered the shape of electrodes, the trajectory of the electrons and the equipotential planes. By keeping in mind all these parameters, the final design of a tetrode type electron gun was decided using SIMION 7 CODE on trial and error method. The electron trajectories and equipotential planes of final design were also checked by LORENTZ SIMULATION CODE. The electrodes have been designed in such a way that the electron beam diameter varies from 5mm to 150 mm.

The configuration of the electrodes, the trajectory of the electrons in the gun and their corresponding equipotential planes for 1 keV and 10 keV electron energies are shown in figure 2.2 (K = Cathode electrode, F = Focusing electrode, C = Control...
electrode and A = Anode electrode). From figure it is clearly observed that, by changing the relative voltages across the electrodes, it is also possible to keep the beam diameter same for different electron energies.

The electron beam diameter, configuration of the electrodes, trajectory of electrons in the gun geometry and equipotential planes were checked for different values of $V_K$, $V_F$, $V_C$ and $V_A=0$, as shown in figure 2.3. To study variation of electron beam diameter, bias voltage of the electrodes $V_K$, $V_F$ and $V_A$ were kept constant and $V_C$ was varied. The change in the electron beam diameter with control electrode voltage, $V_C$ is shown in figure 2.3.

Figure 2.2: The electrodes geometry, trajectory of electrons and equipotential planes in electron gun for 1 keV and 10 keV energy. [Using SIMION 7 CODE]
(a) \(V_K = -5550, \ V_F = -5560, \ V_C = -1020, \ V_A = 0\)

(b) \(V_K = -5550, \ V_F = -5560, \ V_C = -2020, \ V_A = 0\)

(c) \(V_K = -5550, \ V_F = -5560, \ V_C = -3020, \ V_A = 0\)
Figure 2.3 (a), (b), (c), (d) and (e): The variation of electron beam diameter with control electrode voltage, $V_C$, at constant values of $V_K$, $V_F$ and $V_A = 0$.

The variation of electron beam diameter with control electrode voltage, $V_C$, was also studied using LORENTZ SIMULATION CODE. The results obtained from this code are similar to that obtained from SIMION 7 CODE. From these results one can conclude that electron beam diameter decreases with increase in control electrode voltage. The shape of the electrodes, voltage across each electrode and subsequently equipotential lines around the electrodes plays important role in deciding the beam trajectories. Therefore, this type of electron gun one can use in the
studies in which sample area may vary. The variation of electron beam diameter with control electrode voltage, $V_c$ obtained by LORENTZ SIMULATION CODE is shown in figure 2.4.

(a) $V_K = -5550, V_F = -5560, V_C = -1020, V_A = 0$

(b) $V_K = -5550, V_F = -5560, V_C = -2020, V_A = 0$
c) $V_K = -5550, V_F = -5560, V_C = -3020, V_A = 0$

(d) $V_K = -5550, V_F = -5560, V_C = -4020, V_A = 0$
2.5 Electrodes and assembly

The electron gun has four electrodes namely the cathode (K), the focusing electrode (F), the control electrode (C) and the anode electrode (A). Non-magnetic stainless steel material has been used to fabricate the electrodes. The shape of the cathode (K) is made concave which made it easy to focus the electron beam towards the next electrode i.e. focusing electrode. The focusing electrode is cylindrical in shape. This electrode pushes the electrons towards the control electrode. The aperture of the control electrode (C) has conical shaped opening. This electrode provide wide path for electrons. In the anode electrode, the ends, the opening and closing are of same diameter. The electrodes are assembled in a single unit through ceramic rods of suitable length to maintain the desired separation and insulation.

2.5.1 Cathode electrode

Using SIMION 7 code and LORENTZ SIMULATION code, the shape and size of the cathode electrode of the electron gun were decided for the desired electron beam diameter, current and beam uniformity of the electron gun. The cathode has concave shape so that the electrons can be focused towards electrode aperture. The

\[ V_K = -5550, \ V_F = -5560, \ V_C = -5020, \ V_A = 0 \]
radius of curvature of the cathode is 18 mm, axial-hole diameter 4.5 mm and the cathode diameter 62 mm. The 3-D view and mechanical drawing of the cathode are shown in figure 2.5.

**Figure 2.5: The 3-D view and mechanical drawing of the cathode**

### 2.5.2 Focusing electrode

In the same line, SIMION 7 code and LORENTZ SIMULATION code decided the design parameters of the focusing electrode considering the electron trajectories and equipotential planes. The focusing electrode has cylindrical shape with diameter ~ 62 mm axial hole has diameter ~ 20 mm and length 9 mm. This electrode guides the electrons towards the control electrode. The 3-D view and mechanical drawing of the focusing electrode are shown in figure 2.6.

**Figure 2.6: The 3-D view and mechanical drawing of the focusing electrode**

### 2.5.3 Control electrode

Similar to previous electrodes, the design parameters of the focusing electrode were obtained such as to facilitate the focusing or defocusing action on the electron
beam. The control electrode has diameter ~ 62 mm. The control electrode aperture has conical shaped opening. The opening, that faces the focusing electrode, has a diameter of ~ 8.5mm and its backside opening that faces the anode aperture, has a diameter of ~ 11mm. The 3-D view and mechanical design of the control electrode are shown in figure 2.7.

![Figure 2.7](image1)

Figure 2.7: The 3-D view and mechanical drawing of the control electrode

### 2.5.4 Anode electrode

The design of anode electrode was finalized in order make it possible to anode to create easy passage for the electrons without in the intensity. The anode electrode has opening and closing ends are of same diameter ~17mm. The 3-D view and mechanical drawing of the anode electrode are shown in figure 2.8.

![Figure 2.8](image2)

Figure 2.8: The 3-D view and mechanical drawing the anode electrode

### 2.5.5 Assembly of the electron gun

In addition to shape and size of the electrodes, their relative separations were also obtained from SIMION-7 and LORENTZ CODE. The separation between the
cathode and focusing electrode is ~ 8 mm and that is of the focusing electrode and the control electrode is ~ 13 mm. The separation between the control electrode and the anode is ~ 15 mm. Cylindrical ceramic rods clutched the electrodes and provided insulation in between the electrodes. The two dimensional assembly drawing and actual assembly of the electron gun system are shown in figure 2.9 and figure 2.10.

![Figure 2.9: The 2-D assembly drawing of the electron gun](image)

Figure 2.9: The 2-D assembly drawing of the electron gun

![Figure 2.10: A photograph of (a) Electron Gun mounted on acrylic glass flange and (b) Ceramic rods holding the electrodes.](image)

Figure 2.10: A photograph of (a) Electron Gun mounted on acrylic glass flange and (b) Ceramic rods holding the electrodes.

### 2.6 Electron irradiation facility

The electron irradiation system consist (a) stainless steel irradiation chamber (b) electron gun assembly (c) sample holder cum faraday cup (d) silver activated zinc sulphide coated screen and (e) vacuum pumping units.
2.6.1 Actual mechanical design

2.6.1.1 Irradiation chamber

The irradiation chamber is made from a stainless steel cylinder. It has a diameter of 220 mm, length ~ 350 mm and thickness ~ 4 mm. One of the ends of the chamber was closed with the acrylic glass flange carrying the electron gun where as the other end port was closed by the acrylic glass flange carrying the Faraday cup or silver activated ZnS coating. Irradiation chamber has three small size ports, at 45° angles, and two ports making 90° angles. The perpendicular port to the body of the chamber is on the vacuum system and chamber is positioned horizontally on the vacuum system. One of the 45° port is used as the viewing port, and the other two ports holds flange with feed throughs and connectors. The electron gun is fixed on the high voltage feed through, mounted on one of the closing flange of this chamber. A Faraday cup is mounted on the other closing flange of the cylindrical chamber. In order to observe the electron beam from outside, the Faraday cup flange is replaced by an acrylic glass flange coated with ZnS coating.

2.6.1.2 Gun mounting arrangement

Gun mounting arrangement is made on the acrylic glass flange. One end of the chamber is closed with the flange carrying the electron gun with high voltage feed through, while other end port was closed by the flange carrying the Faraday cup or silver activated ZnS coated acrylic glass flange. The acrylic glass flange has high voltage feed through for electrical connection to the electrodes and electron emitting element i.e. filament of the electron gun. A separate feed through at an isolated position from the electron gun feed throughs are fixed to hold an electron gun assembly. Electrical connections were made to all four electrodes. The filament was connected to the transformer. A photograph of the gun mounting arrangement is shown in figure 2.10.

2.6.1.3 Sample holder cum Faraday cup

The Faraday cup act as sample holder and is of rectangular shape. Faraday cup is made from graphite. One plane of the graphite sheet is used for the current measurement and the other side holds an aluminum plate. The sample can be mounted on this aluminium plate. Thus, sample holder cum Faraday cup has graphite
plate on one side and aluminium plate on opposite side. The graphite plate of the sample holder is connected to the picoammeter for the beam current measurements. The sample holder which also acted as Faraday cup is connected to one end of the stainless steel rod which passes through a Wilson seal mounted on the perpendicular port of the chamber. The Faraday cup or the sample mounted on the aluminium plate can be brought in the path of the electron beam. This is possible because the SS rod can be rotated and displaced linearly inside the evacuated irradiation chamber from outside.

![Figure 2.11: A photograph of the sample holder cum Faraday cup [Ref. 17]](image)

Whenever, the sample holder is displaced out of the electron beam trajectory, the electron beam is collected by another plate fitted on glossy acrylic glass plate connected to a picoammeter. Hence, the electron beam current could be measured. One side of the sample holder is used for the sample mounting and the other side graphite sheet is used for the measurement of electron beam current. A photograph of the sample holder cum Faraday cup is shown in figure 2.11.

### 2.6.1.4 Vacuum pumping system

The Vacuum Pumping System consists of HINDHIVAC Rotary Vacuum Pump (ED Series), Diffusion pump (OD Series) and other hardware like valves, baffles, collar, gauge and plumbing lines etc., fully integrated and wired. The Vacuum Pumping System, is trolley mounted for easy movement, are capable of achieving an ultimate vacuum $10^{-6}$ torr. Liquid nitrogen trap is to minimize the backstreaming of oil vapors, and ensures clean and better ultimate vacuum of $10^{-6}$ torr range. The vacuum pumping system was fitted with Pirani Gauge to measure the
roughing and backing vacuum and Penning gauge for measuring the high vacuum. A photograph of the vacuum pumping system is shown in figure 2.12

![A photograph of the Vacuum Pumping System](image)

Figure 2.12: A photograph of the Vacuum Pumping System

### 2.6.2 Electrical and electronic components

#### 2.6.2.1 High voltage power supply

The high voltage power supply used in this system provide adjustable and regulated DC voltage over the range 0 to 30 kV, with maximum current ~1 mA (Model: RHR 30PN30/220). The polarity of the voltage is kept at negative potential and it is directly connected to the cathode of the electron gun. The full load input current of the power supply is approximately 1.5 Amp and 0.8 power factor. The other unique features of this supply are static load ± 0.01% +1V, static line ± 0.01% +1V, ripple factor 0.02%RMS+2V. A resistors-chain is connected across the negative terminal of the power supply and ground. The total value of the resistance was ~ 6000 Mega ohm, hence the current flowing through the chain did not exceed 5 microampere. The applied voltage to the different electrodes of the electron gun bias is provided through the tapping from this chain. The voltage across the electrodes is adjusted to converges or diverges the electron beam from the anode aperture and the desired beam spot [17].

#### 2.6.2.2 Isolation transformer:

To isolate the high voltage supply and main supply, an isolation transformer is used. This isolation transformer operates with AC input voltage 220 V and RMS 50 Hz. The full load input current is approximately 10 Amp. The secondary output
voltage is 40 KV with maximum current 20 Amp. Input of the isolation transformer is connected to main supply through a Dimmer for the fine variation in the voltages.

2.6.2.3 Transformer

In the present irradiation facility, AC to AC converter transformer is used to provide high output current and low output voltage to the filament. The step-down transformer possesses a turn’s ratio of 1:6 and wound on a square former of 70 mm x 80 mm. The primary windings have 60 turns and the secondary of 10 turns were used for the core. The RMS output voltage varies within the range 1 Volt to 30 volt with a current variation of (rms) 1 Amp to 20 Amp. This transformer is connected to Dimmer through isolation transformer. The transformer is connected directly to the secondary of the isolation transformer. In this way, the filament voltage can be varied through a Dimmer.

2.6.2.4 Filament: electron emitting element

The filament is an oxide impregnated tungsten matrix, fixed on the surface of a nickel cylinder. The nickel cylinder has an active surface area of ~ 3.5 mm and length ~ 6 mm. This tiny cylinder is fitted into the cathode electrode of the electrode assembly. A heater is put into the nickel cylinder and two split ends of the heater coil are mounted on the cathode electrode through insulating supports. The surface temperature of the nickel cylinder is changed by varying the voltage across the heater coil.

2.7 Testing of the electron gun and calibration

Ultimately, required parts of the electron beam irradiation facility are (a) electron gun (b) irradiation chamber (c) current meter and (e) vacuum pumping system. The block diagram and photograph of electron irradiation facility are shown in figure 2.13 and 2.14 respectively.
The electron beam diameter depends on the bias voltage of the control electrode. This is shown by the simulation plots in the figure 2.3 and figure 2.4. It shows that the beam diameter decreases with increasing the bias voltage of the control electrode, when $V_k$, $V_F$, and $V_A$ are kept at constant values. Though, it is
possible to keep beam diameter same for different electron energy by adjusting the relative voltages across the electrodes. This is shown in figure 2.2.

2.7.1 Emission current

As mentioned in previous section, the filament is an oxide impregnated tungsten matrix, fixed on the surface of a nickel cylinder. A spiral shape tungsten filament coated with oxide is inserted fully inside the cylinder and was hold in insulating ceramic caps. The filament is connected to secondary of transformer. The primary of this transformer is connected to an isolation transformer. The filament and hence the cathode was heated by applying AC voltage to the primary of the isolation transformer. The emission property of the oxide matrix was studied by varying filament voltage from. After applying the filament voltage, the electron emitting element (oxide impregnated tungsten matrix) started emitting electrons. Furthermore, by applying negative bias voltage to the electrodes, electrons were accelerated. After travelling through the gun geometry, electrons traveled to the Faraday cup. The electron emissive property of the oxide matrix was studied independently by replacing the grid electrode with a small size graphite plate. This grid electrode acted as Faraday cup.

Figure 2.15 shows variations in the electron emission current \(I_E\) with the filament voltage \(V_F\) for three values of the accelerating voltage applied between cathode and the anode plate. The results shown in figure 2.15 specify that the electron emission current \(I_E\) initially increases slowly with the filament voltage upto 13-14 Volts. After these voltages, emission current increases rapidly when the filament voltage \(V_F\) exceeds 15 Volts. These bench test results revealed that even at lower energy (5 keV), a large electron current could be obtained at a filament voltage \(V_F\) greater than 15 Volts. The results show that an electron beam current \(\sim200 \mu A\) can be obtained in the present system.
2.7.2 Electron Beam Current

The Keithley current meter was used to measure the electron beam current. For this purpose, the Faraday cup was mounted on the closing acrylic glass flange of the irradiation chamber. By applying the proper negative potential to the cathode (K), the focusing electrode (F) and the control electrode (C) were made negative with respect to ground potential. The relative potentials were maintained in magnitude order $V_F > V_K > V_C$ and the anode electrode (A) was kept at the ground potential ($V_A$). The electrons interacting to the Faraday cup which is mounted on the closing acrylic glass flange of the irradiation chamber constituted electron beam current ($I_E$) at particular accelerating voltage between the cathode and the anode electrode. The variations in the electron beam current with the electron energy ($E_B$) were studied for different filament voltages.

Figure 2.16 shows variations in the beam current ($I_B$) with beam energy ($E_B$) for different values of filament voltage ($V_f$). It is observed from figure 2.16 that, the beam current ($I_B$) gradually increases with increasing beams energy ($E_B$) at a constant filament voltage. These results indicate that at a given beam energy ($E_B$) the beam current ($I_E$) can be varied over a large range by varying the filament voltage.
voltage \((V_F)\). This type of electron gun is required for special applications, where electron beam current \((I_B)\) can be easily varied.

![Diagram showing variations in beam current \((I_B)\) with beam energy \((E_B)\) for different values of filament voltage \((V_f)\).](image)

Figure 2.16: Variations in the beam current \((I_B)\) with beam energy \((E_B)\) for different values of filament voltage \((V_f)\)

### 2.7.3 Beam diameter

To measure the electron beam diameter, the other end of the irradiation chamber was closed with a flange made of transparent acrylic glass. This acrylic glass was given a conducting transparent coating. The coating was over a circular area of 15 cm diameter. For the preparation of the coating, a thin layer of \(\text{TiO}_2\) transparent conducting coating was coated on the acrylic glass. Moreover, a thin layer of silver activated ZnS was made on \(\text{TiO}_2\) coating. Electrical connection was employed from the conducting coating to a current meter through a BNC connector mounted on the port. Whenever electron beam shine on the silver activated ZnS coating, a blue color glow could be observed through the Plexiglas flange. In this manner, the beam current and diameter measurement was done using standard technique from outside the chamber. It was possible to vary beam diameter from 5 mm to 100 mm by varying the potentials of the respective electrodes of the electron gun.

The beam diameter variations with respect to applied voltages between the electrodes were studied to check the possibility of testing the samples of different sizes. For this purpose, the end port flange of the irradiation chamber was replaced by
a transparent acrylic glass flange coated with silver activated ZnS. The distance between the anode and this silver activated ZnS coated plate was around ~ 200 mm. The electrons diminishing on the ZnS(Ag) coating produce glow inside was seen from the other side of this flange outside the chamber. This made it possible to measure the beam diameter using the standard techniques. The beam diameter could be varied between 5 mm to 120 mm.

Figure 2.17 shows photographs of the three electron beam spots of different diameters recorded from a silver activated ZnS screen made on the acrylic glass flange of the chamber. From three electron beam spots, shown in photograph 1, it can be observed that the circular shape of the beam spot can be maintained even though the beam current ($I_B$) and the beam diameter ($D_B$) are varied.

![Beam Diameter: 30 mm](image1)

![Beam Diameter: 120 mm](image2)

**Figure 2.17: Photographs of beam spots with different diameter**

### 2.7.4 Beam Uniformity

The Faraday cup designed for measuring the beam uniformity consist 200 numbers of small circular graphite cylinders, each of diameter 4 mm and length 5 mm. These graphite cylinders were fitted in the grooves made on a 10 mm thick acrylic glass plate. This acrylic glass plate was used as closing flange and was fixed directly on the irradiation chamber. Each groove had a small hole through which the electrical connection to the graphite cylinder could be made from the other side of the acrylic glass plate. This special type of Faraday cup is shown in figure 2.18. This flange was fitted on the chamber and the system was evacuated to measure the electron beam current. Electron beam was incident on this flange, and the electron gun beam current from each cylindrical Faraday cup was measured. Beam current was measured by using multiplexing electronic systems. Beam current ($I_B$) from each of the graphite Faraday cup mounted along the X-axis was measured. The variations
in the beam current with the position of the graphite cylinder were studied for three different beam energies. In the similar manner, measurements were also made from the graphite Faraday cups mounted along the Y-axis.

Figure 2.18: A view of this special type of Faraday cup [Ref. 17]

The electron density over the beam spot is also measured with a multielectrode assembly and was found to be better than 10%. This level of beam uniformity is sufficient for the electron irradiation experiments for materials science studies and synthesis of nanoparticles in polymer matrix. The variation in the current with the distance from the centre of the beam spot is shown in figure 2.19.

Figure 2.19: Variations in the current ($I_B$) along X-axis over the beam spot at 3 different beam energies.
2.8 Conclusions

This tetrode type electron gun system can provide electrons up to energy of 20 keV and beam current up to 100 µA at all the electron energies. The unique features of this electron irradiation facility is that, at a set value of any electron energy, the electron beam diameter can be varied from 5 mm to 120 mm on silver activated ZnS coated acrylic glass mounted at a distance ~200 mm from the anode of the electron gun. The electron beam current can also be increased up to 100 µA, at the set values of the electron energy and beam diameter. The electron irradiation system with such changeable parameters is requisite in several electron irradiation experiments, where samples of different sizes are necessary to irradiate at different energy electrons, at a uniform current density. The uniformity of the electron beam, over the entire beam area, was measured with a multielectrode assembly and is found to be 13%. The circular shape of the electron beam is maintained even when the beam current, energy and diameter are changed. This electron irradiation system is being used for studying the irradiation effects of 1 keV to 20 keV energy electrons on space quality insulating materials and synthesis of metal nanoparticles.
References:


Part B: Synthesis of silver and gold nanoparticles in PVA matrix by low energy electron irradiation

2.1 Introduction

Synthesis of metal nanoparticles through different routes has become an important area of research and development [1]–[3]. There has been a special interest in the study of metal nanoparticles for its wide range of applications in different fields such as optics [4], electronic [5] and sensors [6]. The nanoparticles of noble metals, such as silver and gold, can exhibit size dependent electrical and optical properties [7], [8]. It is rather difficult to produce nanoparticles in a thin insulating and transparent coating through conventional methods, at room temperature. Metal nanoparticles in an insulating medium can have applications in the fields of nano-engineering [9], nano-electronics [10] and nano-bioelectronics [11].

A number of researchers have carried out work in the fields related to synthesis of metal nanoparticles by different methods such as photochemical [12], [13], electrochemical [14], [15], chemical reduction [16], [17], Radiolysis [18]–[21], microwave processing [22], ultra-sound processing [23], gamma irradiation [24], [25], ion irradiation [26] and plasma processing [27]. In the earlier reported work [28], the particle size of silver and gold particles in the solution is found to decrease with increasing dose rate. The dose rate of gamma rays of Co-60 (1.17 MeV), electrons of 10 MeV, C\textsuperscript{12} ions of 795 MeV and C\textsuperscript{13} ions of 870 MeV are compared. Moreover, the earlier work has been carried out on liquid samples; however, in the present work the samples used are thin films. The electron sources, which can deliver 10 to 40 keV electrons beam are used for various applications such as patterning [29], [30], lithography [31], [32] and MEMS [33], [34], however, the work on the synthesis of metal nanoparticles through keV energy electron-irradiation is important.

This part of the chapter mainly deals with a method of synthesis of metal nanoparticles based on keV electron irradiation. In this study, silver and gold nanoparticles have been synthesized by irradiating silver and gold coated PVA (poly vinyl alcohol) film samples. This method is easy in operation and even period of few minutes is sufficient to obtain the nanoparticles.
2.2 Mechanism

2.2.1 Mechanism of interaction of electrons with polymers

When a polymer is exposed to energetic radiation, the processes such as scissioning and cross-linking of the molecular chains are induced, due to rupture of covalent bonds. The scissioning of the molecular chains leads to formation of free radicals at the end groups of the molecular chains that can either react or split off into fragments of neutral molecules or groups of atoms. At a given temperature, these fragments obey Brownian movement, which can lead to the formation of free volume (empty sites, vacancies) in the polymer matrix. Free volume, produced due to vacancies, plays a very important role in diffusion processes. The free volume must achieve a configuration, which is energetically favorable for the diffusion of atoms in the polymer matrix. The atoms of an element can diffuse into a polymer only when such fluctuations are sufficiently large to fit the element in the available free volume. Thus, in the energy considerations, external atoms can move to successive potentials of local equilibrium. Furthermore, the radicals formed in the matrix during irradiation act as hopping sites for the diffusing atoms. The radiation-assisted diffusion of the atoms of any element in the polymer occurs by means of motion of defects [35].

During irradiation, the steady state concentration of the vacancies and defects, and their build-up time depends on the rate of annihilation of vacancies and defects through different processes. The effective diffusion coefficient, $D'$, under irradiation condition at a temperature, $T$, can be expressed by the following relation [35],

$$D' = D + \frac{R_v}{C_{SR} + C_{ST}}$$

(2.1)

where, $D$, is the thermal diffusion coefficient and $C_{SR}$ is the sink concentration due to radiation and $C_{ST}$, is the sink concentration due to temperature, $T$. At room temperature, $C_{ST}$, and $D$, are negligible and therefore the above relation (2.1) leads to an equation,

$$D' = \frac{R_v}{C_{SR}}$$

(2.2)

Under irradiation conditions, the rate of vacancy production, $R_v$, is proportional to the incident radiation flux. A fraction of the radiation induced vacancies and the free volumes can be occupied by the atoms of the diffused elements, such as Ag or Au. In the present case, the rate of the diffusion is governed
by the net concentration of vacancies existing at that instant in the surface region of
the silver and gold coated PVA films. As the concentration of the diffused metal
atoms in the polymer increases the solubility limit, a process of nucleation and growth
starts, which results in the formation of metal particles of nanometer size.

2.2.2 Mechanism of synthesis of nanoparticles by electron irradiation

During keV electron irradiation, the electron entering into the medium and
transfer its energy to the medium through various processes like ionization, excitation
of atoms, chain-scission, cross-linking, evaporation of molecules, etc. When an
electron beam interacts with PVA mixed metal salt, the following mechanism takes
place [35].

PVA interact with electron generates \([-\text{CH}_2-\text{COH-CH}_2]-_n\), free radical and
simultaneously the metal salt (MX) produce metal ions (M\(^+\)).

\[
\begin{align*}
[ -\text{CH}_2-\text{CHOH- } ]_n & \quad \rightarrow \quad [ -\text{CH}_2-\ddot{\text{COH- }} ]_n + \text{H}^+ + 1\text{e}^- \\
(\text{PVA}) & \quad \rightarrow \quad \text{(PVA radical)} \\
\text{MX} & \quad \rightarrow \quad \text{M}^+ + \text{X}^-
\end{align*}
\]

The electron capture cross section For the M\(^+\) ion is so high, and therefore, a
large number of neutral (M\(^0\)) get easily produced in the solution through the
following reaction

\[
\text{M}^+ + \text{e}^- \rightarrow \text{M}^0
\]

The neutral metal atoms can encounter the excess M\(^+\) ions and produce M\(_2^+\)
species. Thus, progressively leads to the growth of metal nanoparticles in the film
through the following reactions

\[
\begin{align*}
\text{M}^0 + \text{M}^+ & \rightarrow \text{M}^+_2, \\
\text{M}_{n-1} + \text{M}^+ & \rightarrow \text{M}_{n}^+
\end{align*}
\]

Moreover, the reaction leading to the reaction of M\(^+\) ions can be produced
through the strongly reducing hydrated electrons as well as by the polymeric radicals
PVA\(^*\). During electron irradiation, the following chemical reaction can be induced.

\[
\text{M}_{n}^+ + \text{e}^-/\text{PVA}^* \rightarrow (\text{M})_n \quad \text{(Metal nanoparticles)}
\]

In this manner, during electron irradiation, the size of metal particle can grow
and subsequently silver particles of nano matrix dimensions can be synthesized in the
film.
2.3 Experimental

In this study PVA (poly-vinyl alcohol) has been used as a medium to form metal nanoparticles. Thin sheets of PVA (~100 μm) were cut to obtain a number of samples, each of size ~ 15 mm X 15 mm. These samples were stored in a dry atmosphere after cleaning. For diffusion of metal nanoparticles, coating of Ag and Au solutions were made on PVA films. These coatings were irradiated using low energy electrons of different fluences. A detail of preparation of sample is given below.

2.3.1 Preparation of PVA films

The PVA films were obtained using PVA granules. For this, Pure PVA granules (Molecular Weight = 1, 25,000) were dissolved in distilled water. The uniformly mixed water based PVA solution was poured into a Teflon Petri dish and dried it at room temperature for few hours to obtain a thin circular PVA sheet of diameter ~ 10 cm. The PVA sheet was cut to obtain number of samples of size ~ 15 mm X 15 mm.

2.3.2 Preparation of thin coatings of Ag and Au on PVA films

Pure HAuCl₄ powder ~ 340 mg was dissolved into 100 ml ethanol. The solution was stirred for five minutes on a magnetic stirrer at room temperature to obtain homogenous solution called Au-solution. Similarly, ~170 mg of AgNO₃ was dissolved into 100 ml ethanol. This solution was also stirred to obtain homogenous solution called Ag-solution. A few drops of these solutions were spread over PVA films which were prepared earlier having each of dimensions ~ 15 mm X 15 mm and subsequently dried to make the thin coatings of silver and gold respectively. The thickness of the coating was ~ 10 μm.

2.3.3 Electron irradiation

The low energy electron irradiation facility [36] is used for the present study has been discussed in chapter 3. Electron beam of varying electron fluences was used for this study. The irradiation of Ag and Au coated PVA films were carried out in the evacuated irradiation chamber. At a time, one gold or silver coating was fixed on the Faraday cup mounted inside the irradiation chamber of low energy electron irradiation system. After closing the Plexiglass flanges of both ends and making
proper electrical connections, the irradiation chamber was evacuated to a pressure of \( \sim 10^{-6} \) mbar. The mounted coating was then irradiated with electrons of prefixed fluence from 0 to \( 24 \times 10^{15} \) e/cm\(^2\). The size of the electron beam was kept 15 mm and the uniformity was very well within 10\%. The electron beam was turned off as soon as the coating sample received prefixed electron fluence. The irradiation chamber pressure was brought to atmospheric conditions and the electron irradiated coating was removed from the chamber. Other silver or gold coating was mounted on the Faraday cup and the irradiation chamber was evacuated. In this manner, a number of silver and gold coatings were irradiated with 15 keV electrons, by varying electron fluences from coating to coating. The electron current was kept constant for each coating irradiation of low energy electrons.

The radiation dose rate estimated using the expression, \( \phi = \frac{I_0V\times 10^5}{aR\delta} \) rad/s [37], where \( I_0 \) is the inject current in Amp, \( V \) is the beam voltage, \( a \) is the irradiated area in cm\(^2\), \( R \) is the depth in cm and \( \delta \) is the density in gm/cm\(^3\). Since \( R \) increases more than linearly with \( V \), \( \phi \) decreases with increasing electron energy. The radiation dose rate has been estimated and the value is 1.09 kGray/sec corresponding to electron energy 15 keV.

### 2.4 Characterization

To study the presence of nanoparticles synthesized in the PVA matrix, characterization of irradiated samples was needed. For this, different sets of silver and gold coatings irradiated with low energy electrons at different fluences were characterized by the UV-VIS absorption, XRD, SEM and RBS techniques.

### 2.5 Results and discussion

#### 2.5.1 Silver nanoparticles

##### 2.5.1.1 UV-VIS absorption analysis

The UV-VIS spectra of three silver coatings on PVA films irradiated at different fluence from \( 12 \times 10^{15} \) to \( 24 \times 10^{15} \) e/cm\(^2\) is shown in figure 2.1. The characteristic surface plasmon absorption peak of Ag nanoparticles has been an evidence for the growth of Ag nanoparticles in the PVA matrix. The characteristic surface plasmon absorption peak of the Ag nanoparticles in the PVA film at electron fluence of \( 12 \times 10^{15} \) e/cm\(^2\) has appeared at \( \sim 435 \) nm. It is observed from the figure that, the plasmon absorption peak shifted from 435 nm to 404 nm when the electron
fluence is increased from $12 \times 10^{15}$ to $24 \times 10^{15}$ e/$\text{cm}^2$. The shift in the plasmon absorption peak from 435 nm to 404 nm is attributed to the decrease in average size of Ag nanoparticles with increasing electron fluence. This blue shift in the plasmon absorption peak position is also accompanied by an enhancement in the peak intensity. These results, therefore, suggest that relatively small size Ag nanoparticles are produced in PVA matrix at high electron fluence. This is because; particles break into small size nanoparticles at higher electron fluences. In this manner the average size of the Ag nanoparticles gradually decreased and the number of small size Ag nanoparticles increased with increasing electron fluence.

2.5.1.2 X-ray diffraction (XRD) analysis

![Figure 2.1: The UV-VIS absorption spectra of silver coated PVA films irradiated with 15 keV electrons at different fluences.](image)

The X-ray diffraction spectra for virgin silver coating and silver coatings irradiated at the fluence of $12 \times 10^{15}$ e/$\text{cm}^2$ and $24 \times 10^{15}$ e/$\text{cm}^2$ are shown in figure 2.2. From figure it is observed that, the wide diffraction peak at $2\theta = 40.4^0$ corresponds to the PVA crystalline phase and has resulted from the strong intermolecular interactions between the PVA chains through the intermolecular
hydrogen bonding. It is also found from the figure that, only one XRD peak at $2\theta = 38.2^0$, corresponding to (111) plane of face centered cubic Ag, has appeared in the XRD spectra of both the Ag diffused PVA samples. This result shows that the Ag atoms diffused in the polymer matrix have grown into nano-crystallites with preferential (111) orientation. Further analysis of the XRD spectra using Debye-Scherrer’s formula reveals that over the range of electron fluence from $12 \times 10^{15}$ to $24 \times 10^{15}$ e/cm$^2$, the size of the synthesized Ag particles in the PVA film varied from 40 to 20 nm.

![XRD spectra](image)

Figure 2.2: The XRD spectra of silver coated PVA films irradiated with 15 keV electrons at different fluences.

2.5.1.3 SEM analysis

The cross-sectional SEM images of virgin silver coated PVA film and silver coated PVA films irradiated with different fluences have been presented in figure 2.3. Figure 2.3(a) shows SEM of virgin silver coated PVA film and remaining images show the formation of Ag nanoparticles on the surface region of PVA matrix due to irradiation of 15 keV at different fluences showed in figure 2.3(b) $12 \times 10^{15}$ e/cm$^2$, figure 2.3(c) $18 \times 10^{15}$ e/cm$^2$ and 2.3(d) $24 \times 10^{15}$ e/cm$^2$. It is observed from the figures that, some bigger size clusters appear to be produced due to agglomeration of the Ag nanoparticles. It is also found that the size of the Ag nanoparticles is getting
reduced as increase in electron fluence. Typically, at electron fluence $24 \times 10^{15}$ e/cm$^2$, the particle size is less than 50 nm. This result also confirmed in UV-VIS and XRD analysis.

![SEM images of (a) Virgin and 15 keV electron irradiated at different fluences (b) $12 \times 10^{15}$ e/cm$^2$ (c) $18 \times 10^{15}$ e/cm$^2$ (d) $24 \times 10^{15}$ e/cm$^2$ for silver coated PVA films.](image)

2.5.1.4 **Rutherford backscattering (RBS) analysis**

To confirm the diffusion of Ag particles in the surface region of PVA film, the RBS spectrum was recorded. The recorded RBS spectrum for silver coated PVA film irradiated with 15 Kev electrons at fluence of $24 \times 10^{15}$ e/cm$^2$ is shown in figure 2.4. In RBS spectrum, the height of the peak is proportional to the number of diffused Ag atoms and the width is proportional to the depth of diffusion of Ag atoms in PVA matrix. Therefore, the estimated depth of diffusion of Ag atoms in the PVA is $\sim 3 \mu$m at electron fluence of $24 \times 10^{15}$ e/cm$^2$. 
2.5.2 Gold nanoparticles

2.5.2.1 UV-VIS absorption analysis

To investigate the formation of Au nanoparticles in PVA matrix, the absorption spectrum of each film irradiated at electron fluences in the range of $12 \times 10^{15}$ to $24 \times 10^{15}$ e/cm$^2$ was measured and the results are shown in figure 2.5. The characteristics surface plasmon peak of Au nanoparticles is evidenced at $\sim 539$ nm for the gold coated PVA film irradiated at $12 \times 10^{15}$ e/cm$^2$. It is observed from the figure that, the plasmon absorption peak shifted from 539 nm to 530 nm as the electron fluence increases from $12 \times 10^{15}$ to $24 \times 10^{15}$ e/cm$^2$. This blue shift in the plasmon absorption peak is attributed to the decrease in average size of Au nanoparticles with increasing electron fluence. Therefore, this result suggests that, large size Au nanoparticles are produced at lower electron fluence and later on these particles are
divided into small size nanoparticles at higher electron fluences. In this manner the average size of the Au nanoparticles gradually decreased and therefore the number of small size Au nanoparticles increased with increasing electron fluence.

2.5.2.2 X-ray diffraction (XRD) analysis

The X-ray diffraction spectra for virgin gold coating and gold coatings irradiated at the fluence of 12 X 10^{15} e/cm^2 and 24 X 10^{15} e/cm^2 are shown in figure 2.6. From figure it is observed that, the wide diffraction peak at 2\theta = 40.4^0 corresponds to the PVA crystalline phase and has resulted from the strong intermolecular interactions between the PVA chains through the intermolecular hydrogen bonding. It is also found from the figure that, only one XRD peak at 2\theta = 38.2^0, corresponding to (111) plane of face centered cubic Au, has appeared in the XRD spectra of both the Au diffused PVA samples. This result shows that the Au atoms diffused in the polymer matrix have grown into nano-crystallites with preferential (111) orientation. Further analysis of the XRD spectra using Debye-Scherrer’s formula reveals that over the range of electron fluence from 12 X 10^{15} to 24 X 10^{15} e/cm^2, the size of the synthesized Au particles in the PVA film varied from 58 to 40 nm.

![Figure 2.5: The UV-VIS absorption spectra of gold coated PVA films irradiated with 15 keV electrons at different fluences.](image)
2.5.2.3 SEM analysis

The cross-sectional SEM images of virgin gold coated PVA film and gold coated PVA films irradiated with different fluences are presented in figure 2.7. Figure 2.7(a) shows SEM of virgin gold coated PVA film and remaining images show the formation of Au nanoparticles on the surface region of PVA matrix due to irradiation of 15 keV electrons at different fluences showed in figure 2.7(b) $12 \times 10^{15} \text{ e/cm}^2$, figure 2.7(c) $18 \times 10^{15} \text{ e/cm}^2$ and 2.7(d) $24 \times 10^{15} \text{ e/cm}^2$. The presence of Au nanoparticles on the surface region of PVA films can be clearly observed in the SEM images. The Au nanoparticles formed in the PVA matrix have dimensions upto 60 nm. These results clearly support the findings of XRD and UV-Vis absorption spectroscopy.
2.5.2.4 Rutherford backscattering (RBS) analysis

The diffusion of Au atoms in the PVA film under 15 keV electron irradiation was also confirmed. The RBS spectrum of a Au diffused PVA film irradiated at an electron fluence of $24 \times 10^{15}$ e/cm$^2$ is shown in figure 2.8. It is observed from the figure that, the peak with edge at the channel number 982 corresponds to Au. This indicates that Au is present at the surface region of the PVA film. Earlier studies done in other metal atoms diffusion in polymer matrix suggest that the concentration of diffused metal atoms in the polymer surface region increased with increasing electron fluence. Therefore, as shown in figure 2.8 the Au diffused PVA film irradiated at an electron fluence of $24 \times 10^{15}$ e/cm$^2$ shows the higher concentration of Au atoms in the PVA film. The estimated maximum depth of diffusion of Au atoms in PVA matrix at an electron fluence of $24 \times 10^{15}$ e/cm$^2$ is found to be ~ 1.5 µm.
2.6 Conclusion

The results of the present study indicate that low energy electrons can be used for synthesis of metal nanoparticles of different sizes in a polymeric medium. These results lead to a definite conclusion that Ag, Au nanoparticles have been synthesized in surface region of the PVA films by the method of low energy electron irradiation. It is interesting to note that the size of these nanoparticles decreases with increasing electron fluence. It is also observed that Ag and Au atoms could diffuse in the polymer surface at room temperature. Moreover, the results of XRD, UV-Vis, SEM and RBS reveal that low energy electron irradiation technique can therefore be used for synthesis of metal nanoparticles in polymer surface over nanometer range (20 nm to 60 nm) of sizes. The same method can be extended to produce conducting metal tracks in an insulating medium, which has various applications in the field of microelectronics.
References


Chapter 2


[35] K. A. Bogle, “Investigations on the (i) radiation induced surface disorders in c-Si and (ii) synthesis of metal nanoparticles by electron irradiation.”
