Thermionic emission
Thermionic emission corresponding to emission of electrons from metals into vacuum played an important role in the development of electronic valves in the early history of electronic devices. As we will see, it does even today in the semiconducting structures.

Thermionic emission from metal to vacuum
In thermionic emission from metal to vacuum, electrons are thermally excited from below the Fermi level $E_F$ in metal to above the vacuum level $E_{vac}$ outside, as schematically shown in Fig. 4.9.

Once the emitted in few numbers at a temperature $T$ (assumed reasonably low), the electrons in vacuum may be treated as a very dilute non interacting system of particles, obeying the ideal gas behavior, and in thermal equilibrium with the electrons in metal, so that the chemical potential $\mu_{metal}$ of electron in metal may be written as

$$\mu_{metal} = \mu_{ext} + k_B T \log \left[ \frac{n \lambda_T^3}{(2S + 1)} \right],$$

where, $\mu_{ext}$ (the chemical potential of electron in the exterior region in absence of thermionic emission) is zero in vacuum, and the second term is the chemical potential of an ideal gas of electron; $n$ is the density of the electron-gas in vacuum, $\lambda_T = h/\sqrt{2m_e \pi k_B T}$, the so called Thermal de Broglie wave length for the electrons, and $2S + 1 = 2$, arising from electron spin degeneracy. Now by definition, $\mu_{ext} - \mu_{metal} = W$, the work function of the metal. and therefore, one gets

$$n = n_0 e^{-\beta W}, \quad \text{where,} \quad \beta = 1/(k_B T) \quad \text{and} \quad n_0 = 2/\lambda_T^3.$$  \hspace{1cm}(48)

The flux of electrons leaving a flat metal surface is $J = n \bar{v}/4$, where $\bar{v}$ is the mean speed of thermionic electrons in vacuum, and by kinetic theory, for ideal gas obeying Boltzmann statistics, $\bar{v} = \sqrt{8k_B T/(2m_e \pi)}$. This means that the electric charge flux is

$$J_e = eJ = RT^2 e^{-\beta \phi_m},$$

where, $R = 4\pi e m_e k_B^2 / h^3$ and we have defined $e\phi_m = W$. The equation for $J_e$ is known as Richardson-Dushman formula for thermionic emission, and the constant $R$ is called Richardson constant, having an approximate numerical value of 120 Amps./(cm$^2$K$^2$).

Thermionic emission over barrier in semiconductors
Consider now a semiconductor structure comprising of GaAs on the left and Al$_x$Ga$_{1-x}$As on the right as shown in Fig. 4.10. Since the band gap in Al$_x$Ga$_{1-x}$As is larger than that of GaAs, there is a jump in $E_c$ (the conduction band minima) by the $\Delta E_c$ (the band offset); at finite temperature, there is now a possibility of carriers moving from left to right via thermionic emission, in the manner analogous to the thermionic emission in the case of metal to vacuum.
Fig. 4.10: Thermionic emission over barrier in semiconductor structures.

Classically, all the electrons with velocity component in the (+)ve z-direction (perpendicular to the planar interface) propagate from GaAs into Al_xGa_{1-x}As, and all the electrons in Al_xGa_{1-x}As having velocity component in the (-)ve z-direction propagate into GaAs. The electric current density from left (GaAs) to right (Al_xGa_{1-x}As) is

\[ J_{L \rightarrow R} = 2e \int_{-\infty}^{\infty} \frac{dk_x}{2\pi} \int_{-\infty}^{\infty} \frac{dk_y}{2\pi} \int_{k_o}^{\infty} \frac{dk_z}{2\pi} v_z f_o(\vec{k}). \]  

(50)

where the factor 2 comes from electron spin degeneracy, \( f_o \) is the Fermi distribution function, \( v_z = \hbar k_z / m^* \), and \( k_o \) is determined from \( \hbar^2 k_o^2 / (2m^*) = |\Delta E_c| \), with \( m^* \) denoting the DOS effective mass including valley degeneracy if any.

Taking \( f_0 \) in Boltzmann approximation, i.e.,

\[ f_o(\vec{k}) \approx e^{-\beta[(E-E_c^L)-(E_{Fn}^L-E_c^L)]}, \]

where \( E_{Fn}^L \) is the quasi-Fermi level in the left (GaAs), one gets using

\[ E - E_c^L = (m^*/2)(v_x^2 + v_y^2 + v_z^2), \]

and \( v_o = \hbar k_o / m^* \),

\[ J_{L \rightarrow R} = \frac{e}{4\pi^3} \left( \frac{m^*}{\hbar} \right)^3 \int_{-\infty}^{\infty} dv_x \int_{-\infty}^{\infty} dv_y \int_{v_o}^{\infty} dv_z v_z e^{-\beta(E_{Fn}^L-E_c^L)} e^{-\beta m^*(v_x^2 + v_y^2 + v_z^2)/2}, \]

\[ = 2e \left( \frac{m^*}{\hbar} \right)^3 I_1 I_2 e^{\beta(E_{Fn}^L-E_c^L)}, \]  

(51)

where,

\[ I_1 = \int_{-\infty}^{\infty} dv_x e^{-\beta m^* v_x^2/2}, \quad \text{and} \quad I_2 = \int_{v_o}^{\infty} dv_z v_z e^{-\beta m^* v_z^2/2}. \]

The integrals \( I_1 \) and \( I_2 \) can be evaluated easily to get

\[ I_1 = \frac{2\pi k_B T}{m^*} \quad \text{and} \quad I_2 = \frac{k_B T}{m^*} e^{-\beta|\Delta E_c|}. \]

Using these results, one then gets

\[ J_{L \rightarrow R} = R^* e^{\beta(E_{Fn}^L-E_c^L-\Delta E_c)}, \]  

(52)

where \( R^* = 4\pi m^* k_B^2 / \hbar^3 = (m^* / m_e) R \) is the effective Richardson constant.

The current from right (Al_xGa_{1-x}As) to left (GaAs) is obtained in a similar manner as

\[ J_{R \rightarrow L} = R^* e^{\beta(E_{Fn}^R-E_c^R)}, \]  

(53)

where it is tacitly assumed that \( m^* \) is same in left or right media for simplicity.

Suppose now that Al_xGa_{1-x}As is doped with \( N_d \) donors while GaAs is undoped. The quasi-Fermi levels then have different separations from the conduction band edge, so that \( J_{L \rightarrow R} \neq J_{R \rightarrow L} \), resulting in a net current. As the electrons start flowing from Al_xGa_{1-x}As (doped) to GaAs (undoped), region, the current density close to the interface changes with time, which can be determined from the continuity
equation (ignoring generation and recombination effects),

\[
\frac{\partial n}{\partial t} = \frac{\partial j}{\partial z},
\]

assuming that the current flows from Al\(_x\)Ga\(_{1-x}\)As to GaAs region. If further, one assumes that this thermionic current flows only within a certain region, which is of the order of the mean free path \(L_m\) for the electrons because of collisions or scattering, the average velocity is much smaller beyond this region), then using \(\frac{\partial j}{\partial z} = -J_{R \rightarrow L}/L_m\), one gets

\[
e\frac{\partial n}{\partial t} \approx -(R^*T^2/L_m)e^{E_F(t)}.
\]

On the other hand,

\[
n(t) = \int_0^n D(E)dE \frac{e^{E_F(t)}}{E} = n_0^*e^{E_F(t)}
\]

which gives

\[
e^{E_F(t)} = n(t)/n_0^*,
\]

where \(n_0^* = 2/(\lambda_T^*)^3\) with \(\lambda_T^* = h/\sqrt{2m_e^*k_BT}\). Thus

\[
\frac{\partial n}{\partial t} \approx -(R^*T^2/eL_m)n(t)/n_0^* = -n(t)/\tau.
\]

(54)

where \(\tau = eL_mn_0^*/(R^*T^2)\) is a time constant (order of pico second near room temperature). The equation for \(n\) has the solution

\[
n(t) = n(0)e^{-t/\tau},
\]

where \(n(0)\) is the carrier concentration in Al\(_x\)Ga\(_{1-x}\)As at the instant \(t = 0\). This shows that Al\(_x\)Ga\(_{1-x}\)As loses initially its electrons in picoseconds, leaving positively charged donors behind, which then give rise to a potential barrier, slowing down further electron transfer, until the equilibrium is reached and the energy bands are bent at the interface.