Chapter 2

Transport in semiconductor quantum dots and metal nanoparticles

This chapter is attributed to a discussion on electron transport in nanostructures, basically quantum dots and metal nanoparticles. The electronic states in quantum dots are sensitive to the presence of multiple electrons due to the coulomb interaction amongst the electrons. Due to the granular nature of the electric charge, quantum confinement, and the resonant structure associated with this confinement, rich transport phenomena are observed in these nano structures. In case of the bulk materials, the electronic properties are dominated by electron scattering and hence the electrons travel with drift velocity. Therefore, in these materials, the magnitude of current is proportional to the drift velocity and hence to the voltage (Ohm’s law is obeyed). The scattering events that contribute to resistance occur with mean free paths that are typically tens of nm in many metals at reasonable temperatures. Thus if the size of the structure is comparable to the mean free path, then scattering events do not occur and hence the Ohm’s law is not obeyed. Classical mechanics fails to explain the various events occurring inside these nanostructures and hence the phenomena become entirely quantum at the nanoscale. In contrast to quantum wells and wires, quantum dots can be sufficiently small with confinement in all the three dimensions that the introduction of even a single electron is sufficient to dramatically change the transport properties due to the charging energy associated with the extra electron which is called coulomb charging. Further charging can be impeded, because the structure now has a higher electrostatic potential than before a charge was added, leading to the phenomenon of Coulomb blockade. In Coulomb blockade of transport, conductance oscillations are
observed with the addition/subtraction of a single electron to/from a quantum dot. If a small conducting particle is placed in the middle of a tunneling gap between two electrodes, the electrons can tunnel from the first electrode to the second by hopping from one electrode to the small particle and then from the small particle to the second electrode. Such an arrangement is as shown in figure 2.1 where a small metal particle of radius, ‘a’ is placed in between the two electrodes. This simple geometry gives rise to a number of processes for electron transfer, the important ones being Coulomb blockade [1, 2] and resonant tunneling [1, 2].

![Figure 2.1 Arrangement to measure Coulomb blockade](image)

2.1 Coulomb Blockade (CB):

2.1.1 Coulomb Blockade in metal nanoparticles

Here, we consider the situation where the electron hops on to the center particle and then hops off to the second electrode. In case of coulomb blockade, the tunneling rate between the dot and the other electrodes must be sufficiently small. This hopping process is very sensitive to the potential of the center island because the charging energy even for one electron can be quite significant. If the charging energy is greater than the thermally available energy, further hopping is inhibited, leading to a region of
suppressed current in the current-voltage characteristics. Once the applied bias exceeds
the ‘Coulomb Blockade’ barrier the current can flow again. When the potential is again
increased to the point that the particle becomes charged with two electrons, a second
blockade occurs. This process repeats for each number of electron occupations of the
particle and the resulting series of steps in the Current-voltage characteristics is called
the ‘Coulomb staircase’.

In the theory of Coulomb blockade, the basic experimental results are
conveniently discussed in terms of a macroscopic capacitance associated with the
system. The change in electrostatic potential due to a change in the charge on an ideal
conductor is associated with the linear relationship

\[ Q = CV \]  \hspace{1cm} (2.1)

Where \( C \) = capacitance, \( Q \) = charge on the conductor, \( V \) = electrostatic potential relative to
some chosen reference (ground)

If two conductors are considered and they are connected by a d.c source, a charge \(+Q\)
builds up on one conductor and a charge \(-Q\) on the other. Then the capacitance is
defined as \( C = Q/V_{12} \). The electrostatic energy stored in the two conductor system is the
work done in building up the charge \( Q \) on the two conductors and is given by

\[ E = \frac{Q^2}{2C} \]  \hspace{1cm} (2.2)

Similarly, for a system of \( N \) conductors, the charge on the conductor \( i \) may be written as

\[ Q_i = \sum_{j=1}^{N} C_{ij}V_j \]  \hspace{1cm} (2.3)
Where the diagonal values $C_{ii}$ are the capacitance of conductor ‘i’ if all other conductors are grounded.

The energy to charge a capacitor of $C$ farads with an electronic charge is $e^2/2C$ ($e/2C$ in units of V) and the capacitance of a sphere of radius ‘a’ is $4\pi\varepsilon_0 a$ where $\varepsilon_0$ is the permittivity of free space and $\varepsilon$ is the relative permittivity of the medium, V is the potential. Thus the voltage required to charge an island is given by

$$\Delta V = \frac{e}{4\pi\varepsilon_0 a} \text{ volts} \quad (2.4)$$

Taking $\varepsilon=1$ and $\varepsilon_0=8.85 \times 10^{-12} \text{ F/m}$ and $a=1\text{ nm}$, we obtain $\Delta V=0.7V$, with $a=100\text{ nm}$,

$\Delta V=7\text{ mV}$.

Thus the Coulomb blockade should be observable in a very small particle at room temperature, whereas temperatures well below 70 K would be required to observe the effect in a 100nm particle.

In systems of very small conductors, the capacitances approach values sufficiently small that the charging energy given by equation 2.2 becomes comparable to the thermal energy, $k_B T$. The transfer of a single electron between conductors therefore results in a voltage change that is significant compared to the thermal voltage fluctuations and creates an energy barrier to the further transfer of electrons. This barrier remains until the charging energy is overcome by sufficient bias. Coulomb blockade will occur for the charging energy several times greater than the thermal energy and this condition implies that sub 10 nm structures need to be fabricated in order to see clear single electron charging effects at room temperatures. It may be mentioned that it is not difficult to grow insulating films with random metallic clusters on this order to observe
the Coulomb blockade effect at room temperature. This effect was first predicted and observed in small metallic tunnel junction systems. In case of metal nanoparticles of size $\geq 2\text{nm}$, quantum confinement effects can be neglected. The charging energy, $e^2/2C$ due to the transfer of individual electrons is the dominant single electron effect in case of metal tunnel junctions. In 1950, Gorter [3] and Darmois [4] recognized the effects of single electron charging in the conductance properties of very thin metallic films. The thin metal films tend to form planar arrays of small islands due to the surface tension, and the conduction occurs due to the tunneling between these islands. The tunneling electron has to overcome an additional barrier due to charging energy and this results in increase of the resistance at low temperatures. Such discontinuous metal films show an activated conductance of value, $\sigma \approx \exp(-E_c/K_B T)$, similar to the intrinsic semiconductor. Neugebauer and Webb [5] developed a theory of activated tunneling in which this activation energy was the electrostatic energy required to tunnel electrons in and out of the metal islands. This activation energy resembles an energy gap called Coulomb gap.

![Coulomb blockade diagram](image)

**Figure 2.2** A cross-section of Coulomb blockade island structures where Au clusters are embedded in a dielectric medium.

A number of studies have been conducted to explain the phenomena concerning the transport properties of metal clusters or islands imbedded in an insulator that are
contacted by the conducting electrodes. A schematic of such a structure is as shown in figure 2.2 where the Au nanoparticles are embedded in a dielectric medium of Al₂O₃ with Al as the two electrodes. Each metal cluster represents a Coulomb island. Giaever and Zeller [6] studied the differential resistance of oxidized Sn islands sandwiched between two Al electrodes forming Coulomb island down to 2.5 nm diameter. They found the Coulomb blockade phenomenon in one of these samples. Meanwhile Kulik and Shekhter [7] derived a kinetic equation for charge transport based on the tunneling Hamiltonian method. One prediction of this theory was the occurrence of single charge effects in transport through single tunnel junctions rather than islands. The observations of such effects in single tunnel junctions have not been particularly successful due to the environmental phenomena.

In metal tunnel junctions, the tunneling barrier is typically high and thin while the density of states at the Fermi energy is very high. The tunneling resistance is therefore independent of voltage drop across the junction. In case of an ordinary resistor, the flow of charge is quasi-continuous and changes with the change in the electric field. But in case of tunneling, there are injections of single particles which involve several characteristic time scales. The tunneling time is very short of the order of 10⁻¹⁴ sec where the actual time (I/e) between tunneling events is in the mean time of several hundred picoseconds between events. The charge also requires some time to rearrange itself on the electrodes due to the tunneling of the single electron. By considering the facts described, the phenomenon of coulomb staircase effect can be understood by considering an equivalent circuit of the Coulomb island (figure 2.3 & 2.4) which consists of a small metallic cluster coupled weakly through thin insulators to
metal leads. The circuit elements represent the tunnel junctions as parallel combination of the tunneling resistance $R_t$ and the capacitance $C$.

![Circuit Diagram](image)

Figure 2.3 A quantum dot coupled to two leads connected to an external circuit

![Circuit Diagram](image)

Figure 2.4 Equivalent circuit of the device of fig2.3 i.e/of a metallic island weakly coupled with the voltage source through two tunnel junctions of capacitances $C_1$ and $C_2$, $R_{t1}$ & $R_{t2}$ represent the tunneling resistances

If $V_a = \text{sum of the junction voltages} (= \text{applied voltage})$ &

$$C_{eq} = C_1 + C_2 \quad (2.5)$$

then it can be shown that

the threshold voltage value is $|V_a| = \frac{e}{C_{eq}} \quad (2.6)$

For tunneling to occur, $|V_a| > \frac{e}{C_{eq}}$. The Coulomb blockade is the result of the additional Coulomb energy, $\frac{e^2}{C_{eq}}$ which must be utilized by an electron to tunnel into or out of the island. Figure 2.5 illustrates the Coulomb blockade effect for double tunnel junctions where a Coulomb gap of width $\frac{e^2}{C_{eq}}$ has opened at the Fermi energy of the metal island,

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half of which appears above and half below the original Fermi energy, so that no states are available for electrons to tunnel into from the left and right electrodes. The electrons in the island have also no empty states to tunnel to either the junctions until the blockade region is overcome by sufficient bias.

From Heisenberg’s uncertainty relation,

\[ \Delta E \Delta t \geq \hbar \]  \hspace{1cm} (2.7)

Where \[ \Delta E \approx \frac{e^2}{C_{eq}} \]  \hspace{1cm} (2.8)

and \[ \Delta t \approx R_C C_{eq} \]  \hspace{1cm} (2.9)

\( \Delta t \) is the time to transfer charge into and out of the island. Combining the above equations, we get that for the observation of the Coulomb blockade, the tunnel resistance should be very large and given by

\[ R_C \frac{\hbar}{e^2} = 25,813 \ \Omega \]  \hspace{1cm} (2.10)

The Coulomb staircase in the current-voltage characteristics was first observed by Kuzmin and Likharev [8] and Barner and Ruggiero [9] in metallic island structures. In Coulomb staircase behavior of the current-voltage characteristics, the current is essentially zero about the origin and then rises in jumps, giving a staircase like appearance. The subsequent jumps in the I-V characteristics correspond to the stable voltage regimes in which one more electron is added or subtracted from the island. Each
plateau corresponds to a stable region where the number of electrons is fixed in the island (figure 2.6). The step nature in I-V characteristics observed experimentally is not symmetric about the origin. This is due to the presence of unintentional background charges which contributes to an additional charging energy to the Coulomb island. These random charges are difficult to eliminate experimentally and represent severe problems in realizing the practical device technologies based on the single electron effects.

![Figure 2.5 Band structure of a double barrier structure in equilibrium (b) under applied bias](image)

![Figure 2.6 Ideal current-voltage characteristics for an asymmetric double-junction system with and without considering coulomb charging](image)

### 2.1.2 Coulomb blockade in semiconductor QD

A vast array of new phenomena can be observed when the phenomenon of Coulomb blockade is studied in the semiconductor quantum dots. This arises from the fact that due to the presence of strong confinement in the low density limit, the energy scales of the quantized energy levels can be compared with the Coulomb charging energy. As the electron number can also be tuned all the way down to zero, the Coulomb charging energy must actually be considered as the electron number dependent quantity. The charging process is also highly sensitive to the application of
external field due to the strong connection of single electron charging to the eigen states of the semiconductor quantum dots. The single electron tunneling in these systems is a powerful tool of the researchers to study the discrete energy spectra with accuracy. To study the effect, the energy spacing of the discrete states comprising of the allowed energy states in the dot should be counted [figure 2.7(a)].

The total ground state energy in a dot of ‘n’ electrons is the sum of the filled single-particle energy states and the electrostatic energy due to the filling of the dot with electrons given by.

\[ E(n) = \sum_{i=1}^{n} E_i + E(n_1, n_2) \] (2.11)

\( E_i \) are the discrete single-particle energies of the quantum dot and \( E(n_1, n_2) \) is the total charging energy of the system due to tunneling from the left and right barriers.

The electrochemical potential in the dot is the energy difference associated with the removal of one electron from the dot and is given by,

\[ \mu_d(n) = E_i(n) - E_i(n - 1) \] (2.12)

In the linear response regime, the applied voltage, \( V_a \) is small and the charging energy does not depend on which the barrier electron tunnels through. For a given gate bias voltage \( V_g \), if the chemical potential \( \mu_d(n) \) which corresponds to the addition of an electron to the dot with \( n-1 \) electrons, lies between \( \mu_l \) and \( \mu_r \) of the reservoirs, the tunneling may occur [figure 2.7(a)]. The system goes from \( n-1 \) to \( n \) and then again to \( n-1 \) alternately, giving rise to the current [figure 2.7(b)]. The conductance, \( G \) vanishes until the level \( \mu_d(n + 1) \) lies between the Fermi energies of the reservoirs, and a new conductance peak appears (fig 2.7b). The period of Coulomb oscillations is constant and
it can be shown theoretically that there is an additional contribution to the Coulomb oscillation peak spacing, which arises from the non-zero energy separation of their \(n\)th and \((n+1)\)th quantized levels. The gate period corresponding to these two successive conductance peaks is,

\[
\Delta V_g = \frac{C_g E_{n+1} - E_n}{C_g e} + \frac{e}{C_g}
\]

(2.13)

where \(V_g\) is the gate voltage and \(C_g\) is the gate capacitance. The second term in the r.h.s of equation 2.13 corresponds to the constant period of the coulomb oscillations which is also an important term in case of metallic single electron transistor. The above equation shows that there is an additional contribution to the coulomb oscillation peak spacing, which arises from the non-zero separation of their \(n\)th and \((n+1)\)th quantized levels.

Figure 2.7: representation of the conductance peak (b) in a semiconductor double-barrier island structure (a) where discrete states co-exist with the Coulomb gap

2.2 Resonant Tunneling:

In the description of Coulomb blockade, the charging of the central particle is treated classically, requiring the quantization of the electronic charge. The condition of the
Coulomb blockade is that the electron localize on the quantum dots and for this for this to happen, the tunneling resistance of the contacts must exceed $\frac{h}{e^2}$. However, the system can be treated quantum mechanically if the coupling between the electrodes and the dot is stronger than this value. The model for double junction is given in figure 2.8 where the central particle has been modeled by considering square well potential of width 2R with the first bound state energy $E_o$. By denoting the tunneling rate from the left of the barrier to the localized state as $\Gamma_L$ and that from the localized state to the right barrier as $\Gamma_R$, the following expression is obtained for the zero-bias conductance [1]

$$G = \frac{4e^2}{h} \frac{\Gamma_L \Gamma_R}{(E-E_o)^2 + (\Gamma_L + \Gamma_R)^2} \quad (2.14)$$

When the incident electron has the same energy as the localized state in the barrier, $E=E_o$ then

$$G = \frac{4e^2}{h} \frac{\Gamma_L \Gamma_R}{(\Gamma_L + \Gamma_R)^2} \quad (2.15)$$

For a symmetric structure such that $\Gamma_L = \Gamma_R$, from equation 2.15 we have the value of conductance, $G_{max} = \frac{e^2}{h}$

2.2.1 Resonant Tunneling in semiconductor QD

We now consider a device structure as in figure 2.1 but with the metal np replaced by a semiconductor QD. The potential energy variation over such a device is given in figure 2.8. The energy band diagram of the device for increasing forward bias starting from zero value and the corresponding I-V characteristics are given in figures 2.9 and 2.10 respectively.
Figure 2.8 One-dimensional potential energy barrier model for resonant tunneling

Figure 2.9 Energy band diagrams of the double-barrier resonant-tunneling structure (a) at equilibrium with Fermi energy $E_F$ & bottom of the conduction band $E_C$ (b) in-resonance (c) off-resonance, $E_C^{\text{em}}, E_C^{\text{oval}}$ denotes the bottom of the conduction band under electric bias for the left & right electrodes, respectively.
The phenomenon of resonant tunneling can be explained as follows:

The process of transport and the resonant tunneling cannot occur when the voltage through the device is very small. Because, under this condition the energy level in the well cannot be in resonance with the Fermi level of the contact and hence no transport of electrons from the left to the right. The transmission coefficient and the electric current through the device increases sharply with increase in applied voltage from zero. The increase in current with the increasing voltage continues reaching the maximum value when the first allowed energy level of the well $\varepsilon_1$ coincides with $E_F$. For further increase in applied bias, $\varepsilon_1$ gets shifted downward below the lower level of conduction energy band of the emitter $E_{e}^{em}$. For further increase in applied bias, $\varepsilon_1$ comes down below the conduction band of the left electrode and hence current decreases due to off-resonance condition. Consequently, the current-voltage characteristic of the diode exhibits a negative differential region (Figure 2.10). At larger bias, further increase of current can be realized due to shifting of the other quasi-bound states energy downward so that they are in resonance with the electron energies in the emitter.

![Figure 2.10](image)

Figure 2.10 I-V characteristics of the Resonant Tunneling Diode having energy band structure of figure 2.9
The first experimental evidence for the resonant tunneling in double barrier structure was reported by the IBM group in MBE structures [10]. Sollner et al. [8] reported pronounced negative differential region in low temperatures I-V characteristics in a double barrier structure. The current corresponding to the NDR is a very important factor since it controls many features of a device. Hence, Peak to Valley ratio (PVR) is an important figure of merit for many applications. The valley current refers to the minimum current following the peak current as the magnitude of the voltage increases.

2.2.2 Resonant tunneling in metal nanoparticles

The phenomenon of resonant tunneling is also exhibited by the metal nanoparticles. In this case also similar to that described above, it can be said that at resonance, $E_F = e_1$ and the localized state is acting like a metallic channel that connects the left and the right electrodes. The resonant tunneling can be described as the electron delocalization on a lattice of the metal atoms. If the value of $R_t$ (eq 2.10) is less than $\frac{\hbar}{e^2}$, the coupling between the metal atom and the atoms of the electrodes would be tight and the phenomenon of resonant tunneling will occur. In the limit of very tight coupling, a molecule in a metallic gap can be considered as mediating resonant tunneling if the states lie close to the Fermi level of the metal. As resonant tunneling is due to the quantization of energy, resonant tunneling may be observed in metal nps of size $\sim 2$ nm for which quantum confinement is effective. For metal nps of size $\geq 2$ nm, $RT$ will not be observed as the energy levels spacing has to exceed the thermal energy ($\sim 26$ meV).

It is worth-mentioning that the environment plays an important role in case of Coulomb blockade. Electron acceptors often have their coulomb energy lowered by
significant polarization of the environment. For resonant tunneling in real situation, the actual potential contains contributions from the ionized dopants, free carriers, and the applied bias in addition to the band offsets of the heterojunctions.

Synthesis processes for semiconductor QDs and metal nanoparticles are described in the next chapter.

References: