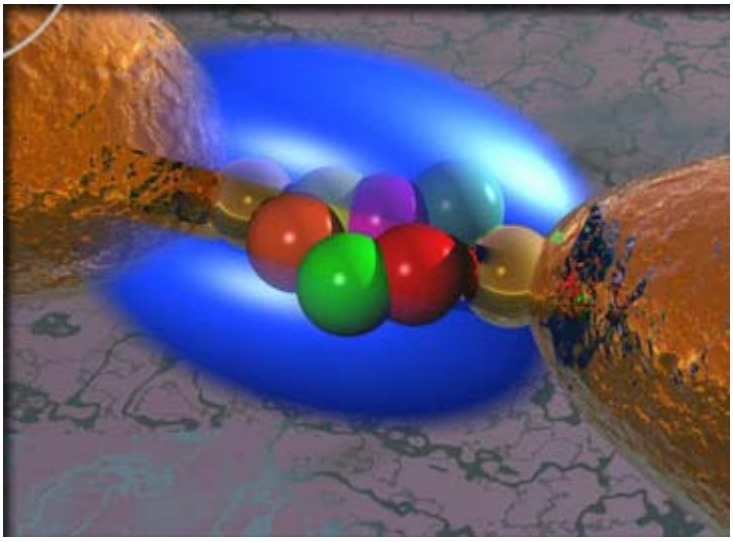
Frontiers in

Nanoscale Science I



- Molecular Electronics -

1. Introduction

"There is plenty of room at the bottom…" – Prof. R.P. Feynman

Miniaturization, a simple thought at the time has now led to ground-breaking advances encompassing every facet of modern life. This scaling of components has brought about a paradigm change in especially the field of electronics, communication and automation along with the discovery of some fascinating science. Major developments have been made particularly due to the extensive downscaling of Silicon based transistor circuitry which led to smaller, faster and efficient devices. Such advances have resulted in a new generation of electronic devices with feature lengths in nanometer scales and thus giving birth to the challenge of nanotechnology. Limitations, both on technological and fundamental scientific ground have however stemmed further development of size and performance of Silicon based electronics.

The discernment of this issue has triggered widespread research on alternative materials and technologies. Developments of methods based on electronic spin, photonic and plasmonic transport are being studied extensively. However, such methods require a deviation from the well established Field Effect Transistor (FET) architecture. Molecular electronics provides a promising solution to this problem by not only retaining the FET architecture but also providing different materials with better intrinsic properties which function with lower energy consumption.

Electrical transport across single molecules is remarkably different from conduction in bulk conductors/semiconductors. In the latter case charge carriers move with a mean drift velocity ν_d, which is proportional to the electric field, E (Ohm's law). For single molecules however this model breaks down. Instead of considering drift velocities and resistances which are only defined as average over a large number of charge carriers, concern here is centered on the transmission of electrons across the molecule. In the present lesson we shall explore how this difference in charge transport can be put to use towards applications which one could envision replacing the current silicon based electronic devices. The following write-up is organized in a way to elucidate the fabrication and functioning of molecular devices analogous to conventional devices.

2. Conventional vs. Molecular devices

Molecular-scale devices under research today include: FETs, junction transistors, diodes, and, molecular and mechanical switches. Logic gates with voltage gain have been built, and many techniques have been demonstrated to assemble nanometer wide wires into large arrays. Programmable and non-volatile devices which hold their state in a few molecules or in square nanometers of material have been demonstrated. In order to elucidate the differences in the fabrication and mechanism of operation of molecular devices compared to their conventional counterparts, a few basic conventional devices and their realization in a molecular scale shall be illustrated here.

2.1 Diodes

The most basic property of a junction diode is that it conducts an electric current in one direction and blocks it in the other. The typical I-V characteristic of a diode is shown in figure 1.

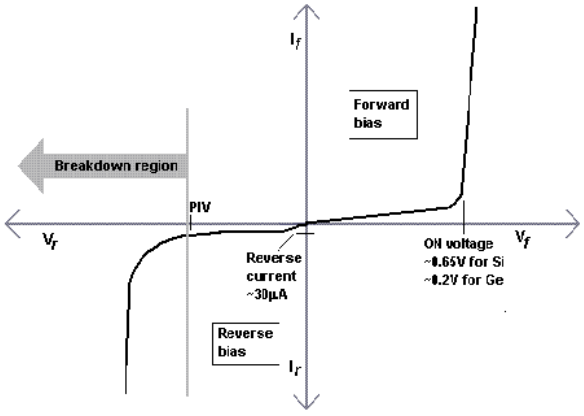


Figure 1. I-V charactertistics of a conventional diode using Silicon or Germanium

It can be seen that upon application of a positive bias voltage the diode allows the conduction of current and completely inhibits the current flow upon application of a negative bias. This property of the diode enables its usage as voltage rectifiers.

2.1.1. Conventional realization

The conventional diode is fabricated using a *p*-*n* semiconductor junction. *P*-*n* junctions are formed by joining *n*-type and *p*-type semiconductor materials, as shown below. Since the *n*-type region has a high electron concentration and the *p*-type a high hole concentration, electrons diffuse from the *n*-type side to the *p*-type side. Similarly, holes flow by diffusion from the *p*-type side to the *n*-type side. If the electrons and holes were not charged, this diffusion process would continue until the concentration of electrons and holes on the two sides were the same, as happens if two gasses come into contact with each other. However, in a *p*-*n* junction, when the electrons and holes move to the other side of the junction, they leave behind exposed charges on dopant atom sites, which are fixed in the crystal lattice and are unable to move. On the *n*-type side, positive ion cores are exposed. On the *p*-type side, negative ion cores are exposed. An electric field Ê forms between the positive ion cores in the *n*-type material and negative ion cores in the *p*-type material. This region is called the "depletion region" since the electric field quickly sweeps free carriers out, hence the region is depleted of free carriers. This separation of charges at the *p*-*n* junction constitutes a potential barrier. This potential barrier must be overcome by an external

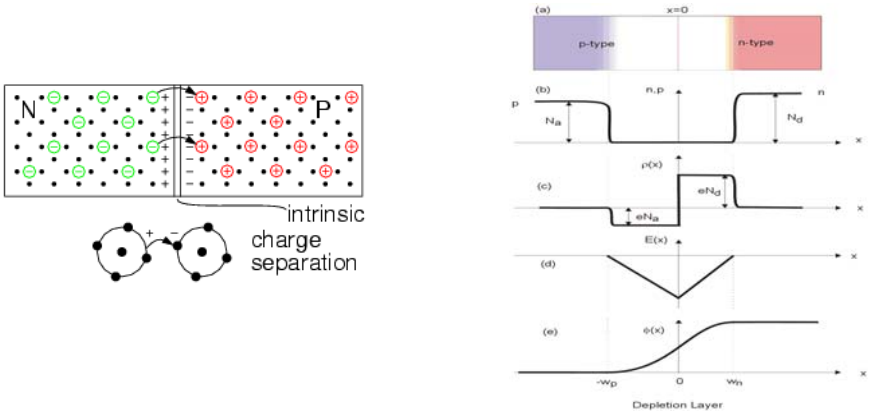


Fig 2 Formation and working of a *p*-*n* junction

voltage source to make the junction conduct and insulate depending on the bias as depicted in figure 3. The formation of the junction and potential barrier happens during the manufacturing process. The magnitude of the potential barrier is a function of the materials used in manufacturing. Silicon *p*-*n* junctions have a higher potential barrier than germanium junctions.

2.1.1. Molecular realization

As explained earlier, a *p-n* junction is required in order to realize a diode. To create a molecular *p-n* junction one would require two different kinds of molecules. The *p*-type component would have to be a molecule which is an electron acceptor and the *n*-type would then be a molecule which is an electron donor. This can be practically achieved by changing the *pi* electron densities of an organic molecule and thus creating an electron rich (*p-type)* or electron deficient (*n-type*) molecules (or molecular subunits). However in molecules the presence of discrete energy levels (refer: HOMO and LUMO) requires the presence of an insulating barrier between the *p-type* and *n-type* molecules. This ensures that the molecular levels do not couple as the HOMO of the donor and lies close to the Fermi level where as the LUMO of the acceptor is close to it as well and a direct junction would result in a charge balance by overlapping of these levels.

Now that we have established the basic components required for a molecular diode, (viz., an electron rich molecule, an electron deficient molecule and a tunneling barrier) the practical realization of these components as a diode will be explained using the well known Aviram-Ratner concept as illustrated in figure 4 [1].

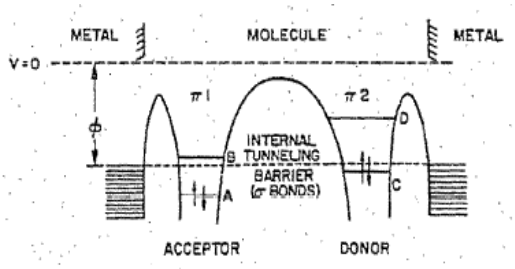


Fig 4 The Aviram Ratner model of a molecular diode

A single molecule could be used as a molecular rectifier if it has an acceptor component and donor component separated by a non conducting part. This can be realized in some organic molecules like the ones shown in figure 5 where the insulating tunneling barrier is realized by using a sigma electron system between the donor and acceptor pi systems.

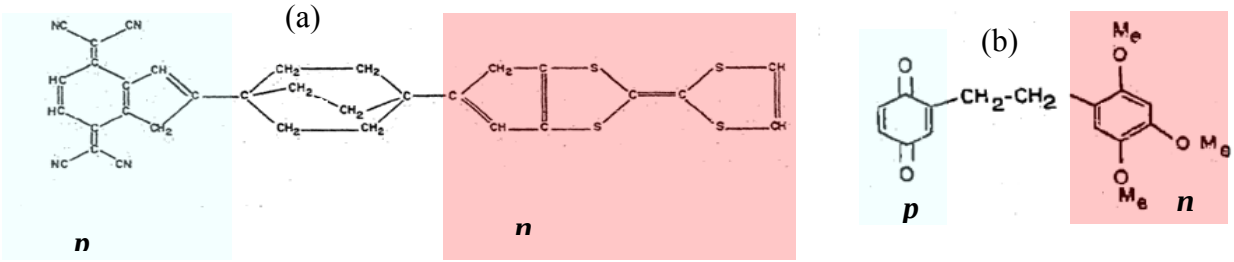


Figure 5. Examples of molecules that could be used as *p-n* junctions. Shaded regions indicate donor and acceptor subparts respectively.

Rectification in such molecules occurs due to the existence of these tunneling barriers. In other words if a voltage is applied to the diode electrons can flow easily across the acceptor and donor. However when the polarity of the applied voltage is reversed the much higher voltage is necessary to allow electrons to flow across the donor and acceptor. This phenomenon is critical to the rectification process and its mechanism shall be explained in detail using an energy level diagram in figure 6.

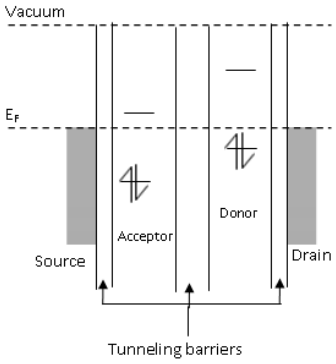
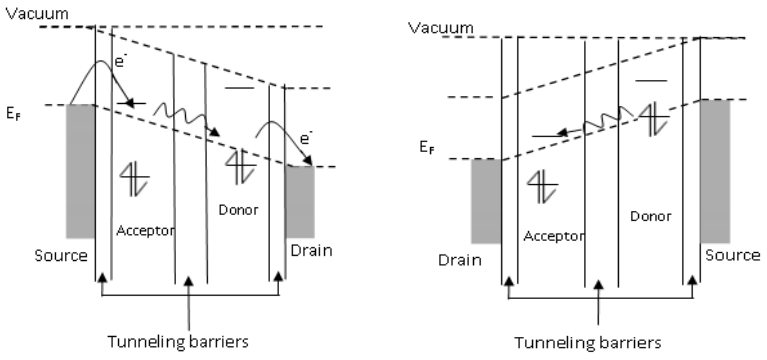


Figure 6 Zero bias condition of an Aviram-Ratner diode

The energy level diagram in figure 6 shows the acceptor having a high electron affinity (LUMO adjacent to the Fermi level) and the donor having a low ionization potential (HOMO close to Fermi level). For proper rectifier behavior the LUMO of the acceptor must be either partially or fully empty and slightly above the Fermi level of the electrode. This picture becomes clearer by observing the changes in the energy level diagram upon application of a bias.



(a) (b)

Figure 7 Working of an Avriram-Ratner diode under (a) forward bias and (b) reverse bias conditions

Upon application of a forward bias (figure 7 (a)), the occupied levels of the cathode and the LUMO of the acceptor overlap as soon as the applied field becomes large enough for the electron tunneling to occur. This depends on the electron affinity of the acceptor molecules. A similar situation will be observed at the donor end of the diode and the applied bias field enables an electron transfer from the donor HOMO to the drain electrode. This electron transfer leaves a hole in the HOMO of the donor molecule. An inelastic tunneling process from the now occupied LUMO of the acceptor occurs to compensate for this hole thus bringing the system to equilibrium. In such a manner the molecular diode conducts electrons under forward biased conditions.

Under a reverse applied bias the energy levels align as shown in figure 7 (b). The LUMO of the donor would be lowered to the Fermi level of the source electrode and the Fermi level of the drain electrode would be lowered to the HOMO of the acceptor. It can be seen here that the threshold field required for the levels to align equivalent to the forward bias situation is higher. Thus electron conduction would require higher fields. Hence for low fields (biases) this system can be considered as a rectifier. However as indicated in figure 7 (b) there may be an alternative mechanism of conduction which involves an internal tunneling from the HOMO of the donor to the LUMO of the acceptor. This process also involves a threshold field due to the intrinsic nature of the acceptor and donor molecules the HOMO of the donor is located energetically below the LUMO of the acceptor and for small fields this system still yields rectification.

The above explained mechanism of molecular diode rectification is the well known Aviram-Ratner ansatz proposed in 1974. This theoretical description however, hides the complexity and difficulties that must be overcome in order to contact a single molecule. The strategies for molecular contacts and some key examples are provided in the following section.

2.1.3. Molecular contacts

The main concept behind contacting a single molecule is to use specifically designed molecular anchoring groups to bind and self-organize on the contacts- that is, must provide a chemical bond to the contacting metal. The nature of the contact determines how strongly the molecular states couple with the electronics states of the electrodes. Stronger the coupling the easier it will be to transmit electrons across the molecule and hence lower resistances. Weakly coupled contacts can provide new effects such as coulomb blockades which may be exploited for new devices (See section 2.3 SET). Thus the choice of the molecular contact is a key issue in the design of a molecular device.

One of the most common strategies for contacting molecules is the utilization of the strong gold-sulfur bond. Besides gold, sulfur also binds to silver [2] or palladium [3]. Sulfur may also be replaced by selenium [4], which yields higher electronic coupling . There are many more systems which have been studied for stronger or weaker coupling like dithiocarbamates [5] , cyanides [6], silanes [7] etc.

There have been many experimental setups to contact single molecules like nanogaps and scanning probe methods. Discussed below are few of the elegantly realized experiments for molecular contacts.

Mechanical controlled break junctions: The concept was first used to obtain superconducting tunnel junctions [8] and later applied to contact a single molecule between two gold electrodes. Here, a metallic wire, which is thinned in the middle, is glued onto a flexible substrate. In many cases the wire is under etched so that a free standing bridge is formed. Underneath the substrate , a piezo element can press the sample against two countersupports which causes the substrate to bend upwards such that a strain is induced in the wire. If the strain becomes too large, the wire breaks and a small tunneling gap opens up between two parts of the wire. The length of the tunneling gap can be precisely controlled by the position of the piezo element. To contact a single molecule, either solution of the molecule is applied to the broken wire or, the molecule are preassembled on the wire before it is broken. The molecules can be bound to the broken ends by using thiol linkers to bind to the gold wire ends and close the tunneling gap, if the length of the gap is accurately adjusted. Thus, using this method one can make a correlation between the molecule and its current versus voltage characteristics and hence this technique is a reliable way to make single molecule devices. [9]

Electromigration: An alternative approach to create a nanogap in a thin metal wire is electromigration. The preparation of the nanogap starts with the definition of a thin metallic wire on an insulating substrate. Molecules are then deposited on top of this wire by self assembly in a solution of the molecules. Subsequently a voltage is ramped across the wire. If the current that flows through becomes too large, the wire breaks due to electromigration which can be detected by a drop in current. Such gaps are approximately 1nm in width and it can be bridged easily as described earlier. [10,11]

Scanning Tunneling Microscopy: Due to its high spatial resolution STM is well suited to contact single molecules. In this method, a gold STM tip is moved on to a gold substrate and slowly retracted. Thereby, a thin gold filament is formed between the tip and the substrate. If the tip is moved far away from the substrate the filament will break and a small tunneling gap is

opened between the substrate and the tip. The whole setup is then immersed in a solution of molecules that have functional binding groups at both ends. If the tunneling gap is approximately the size of the molecule then the gap can be bridged by the metal-molecule bonds as described earlier [12]. Alternatively, the molecules of interest can be embedded into a self assembled monolayer of insulating alkanethiols. In this way it is possible to obtain single, isolated molecules which protrude from the surrounding SAM. The conductance of the molecule can be measured either placing the STM tip above the molecule.[13,14]

Sandwich Structures: In this method a small number of molecules (several thousand) are sandwiched between two metallic contacts. Firstly e-beam lithography and following plasma etching are used to open a pore in a suspended SiN membrane. The pore takes a bowl shape with the opening at the upper edge having a diameter of ~30 nm. Gold is evaporated from the bottom side to fill the pore. The typical crystallite size for gold is about 50 nm and thus the upper surface of gold in the nanopore is probably a single crystallite. The samples are then immediately immersed into a solution of the organic molecules. The molecules if chosen carefully will self-assemble onto the gold surface and form a highly ordered monolayer. After the formation of the layer top electrode is deposited thus contacting the molecules. The I-V characteristics can then be studied by supplying a bias accross the top and bottom electrodes [15].

In terms of integration, the crosswire sandwich structures are quite interesting. In order to obtain a crosswire setup, parallel metallic wires are deposited onto an insulating substrate. A monolayer of molecules is then self-assembled on top of these wires. Metallic wires are then deposited on to this monolayer orthogonally to the bottom electrode wires thus forming the device [16].

Carbon nanotubes: This unique allotrope of carbon, when tailored precisely can form quite robust molecular contacts. The strategy for attaching molecular wires to CNT electrodes is to cut them by local oxidation, leaving two ends that are capped with the product of this oxidation and separated by a molecular-scale gap. These point contacts react with molecules derivatized with amines to form molecular bridges held in place by amide linkages. These chemical contacts are robust and allow a wide variety of molecules to be tested electrically.[17]

A working molecular diode: The Aviram-Ratner concept, although very elegant is however an ansatz. To fabricate such a diode experimentally, mechanically controlled break junction was used to contact molecules with weakly coupled pi systems. The rectification behavior was shown

by the asymmetric nature of the I-V curves. Upon varying the bias voltage it was observed that a higher current was recorded at positive bias when compared to negative bias which is indicative of rectification. The step like features observed in the I-V was attributed to level crossings of the charge carriers in the molecules.

In order to understand the features of the aforementioned molecular diode characteristics, let us revisit the mechanism of charge transport through the molecule. As explained earlier the molecular levels are separated from the electrode levels by a tunneling barrier. So it is natural that the charge carriers tunnel through these barriers to and from the molecules. The tunneling processes however significantly differ when the device is operated in the high bias regime and the low bias regime. In the latter the transmission coefficient of the electron tunneling is less than one. When a high bias is applied the source and drain electrodes align with the molecular levels in a way to allow resonant tunneling (transmission coefficient ~ 1). Therefore each time the electrochemical potentials of the source/drain aligns with a molecular levels the current rises sharply (steps in the I-V).

Although recent advances have been impressive, a basic question that remains a subject of debate is what is the resistance of a simple molecule, such as an alkane chain, covalently attached to two electrodes? Large disparities have been found between different experiments, which reflect the difficulty of forming identical molecular junctions. Even if the resistance of a molecular junction is reproducibly measured, ensuring that the resistance is really due to a single molecule is another substantial challenge. Xu et al showed a simple and unambiguous measurement of single-molecule resistance, achieved by repeatedly forming thousands of molecular junctions in which molecules are directly connected to two electrodes [12]. They created individual molecular junctions by repeatedly moving a gold scanning tunneling microscope (STM) tip into and out of contact with a gold substrate in a solution containing the sample molecules (4,4′ bipyridine and N-alkanedithiols). During the initial stage of pulling the tip out of contact with the substrate, the conductance decreased in a stepwise fashion, with each step occurring preferentially at an integer multiple of conductance quantum G0 − 2e2/h. A histogram constructed from 1000 such conductance curves shows pronounced peaks at 1 G_0, 2 G_0, and 3 G_0. This value is the well-known conductance quantization, which occurs when the size of a metallic contact is decreased to a chain of Au atoms. When the atomic chain was broken by pulling the tip away farther, a new sequence of steps in a lower conductance regime appeared in the presence of the molecule. The histogram now showed peaks at 0.01 G_0, 0.02 G_0, and 0.03 G_0. These conductance steps can be attributed to the breaking of the gold contact and the formation of stable molecular junctions. The

corresponding conductance peaks at 1×, 2 ×, and 3× 0.01 G0 to one, two, and three molecules, respectively, in the junctions. These measurements were repeated for hexanedithiol, octanedithiol, and decanedithiol and peaks in the conductance histograms, were found to occur at different conductance values indicating the different resistances of these molecules.

2.2 Transistors

In electronics, a transistor is a semiconductor device commonly used to amplify or switch electronic signals. A transistor is made of a solid piece of a semiconductor material, with at least three terminals for connection to an external circuit. A voltage or current applied to one pair of the transistor's terminals changes the current flowing through another pair of terminals. Because the controlled (output) power can be much larger than the controlling (input) power, the transistor provides amplification of a signal. The transistor is the fundamental building block of modern electronic devices, and is used in radio, telephone, computer and other electronic systems. Some transistors are packaged individually but most are found in integrated circuits. In this section a detailed description of the concepts involved in conventional transistors (Field Effect Transistors in particular) and their molecular realization shall be discussed.

2.2.1. Conventional Field Effect Transistor (MOSFET)

Today's conventional FETs are based on the Metal-Oxide-Semiconductor model as depicted in figure 8. The FET structure essentially consists of a semiconducting substrate (a traditional metal–oxide–semiconductor (MOS) structure is obtained by depositing a layer of silicon dioxide (SiO2)) and a layer of metal (polycrystalline silicon is commonly used instead of metal) on top of a semiconducting material into which two degenerately doped (discussed later) regions are formed (for example by ion implantation) which form the source and drain electrodes. As the silicon dioxide is a dielectric material its structure is equivalent to a planar capacitor, with one of the electrodes replaced by a semiconductor.

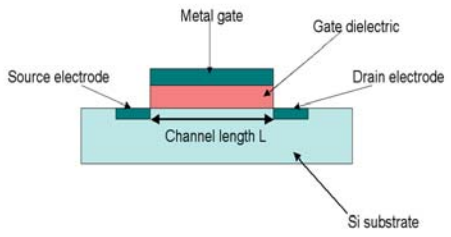


Fig 8 Components of a conventional Field Effect Transistor

To understand the working of the FET let us revisit some of the basics of capacitive effects. A basic capacitor is made up of two conductors separated by an insulator, or dielectric. Upon application of a voltage across it charges accumulate at the ends of the dielectric forming an electric field in the dielectric. The extent of this charge accumulation depends on the capacitance of the dielectric defined as $C= \varepsilon A/d$ (ε = permittivity of the dielectric, A = area of crossection of the capacitor, d= thickness of the dielectric). In a semiconductor MOSFET, a voltage is applied at the metal gate, hence introducing an electric field across the gate dielectric. For example, if a positive bias is applied to the gate, it attracts the electrons in the semiconductor towards the semiconductor- dielectric interface thus forming a conducting channel for the transport of electrons. The picture becomes clearer if this situation is analyzed the changes in the semiconductor bands. In the absence of a bias the Fermi levels of the semiconductor and the drain-source contacts are energetically separated. Application of a bias shifts the Fermi level of the semiconductor to energetically higher or lower levels. At sufficient gate bias the Fermi level is raised above the conduction band edge at the semiconductor insulator interface allowing an excess of electrons to be present. The source-channel-drain path is electron rich now allowing a current to flow. In digital circuits the switching operation is between two values of gate bias corresponding to conduction or no conduction between the source and the drain.

Doping "complementary semiconductors": The semiconducting material used for fabrication of the FET can be tailored according to the necessities of the application. This modification, known as *Doping* of the semiconductor is the process of intentionally introducing impurities into an extremely pure (also referred to as intrinsic) semiconductor to change its electrical properties. The impurities are dependent upon the type of semiconductor. Lightly- and moderately-doped semiconductors are referred to as extrinsic. A semiconductor doped to such high levels that it acts more like a conductor than a semiconductor is referred to as degenerate. For FET based application one dopes the semiconductor lightly to obtain either a *p*-type or an *n*-type semiconductor.

In order to obtain a *p*-type semiconductor one has to dope the intrinsic semiconductor using acceptor atoms like Boron which take up an electron from the semiconductor and leaves extra holes. This results in a shift of the Fermi level close to the valence band due to the creation of extra hole energy levels. By doping the intrinsic semiconductor with donor atoms like Arsenic, one can shift the Fermi level close to the conduction band due to the creation of extra electronic energy levels thus creating an *n*-type semiconductor.

CMOS-Complementary Metal Oxide Semiconductors: One of the applications of doping of semiconductors is for the fabrication of logic circuits. CMOS uses complementary and symmetrical pairs of p-type and n-type metal oxide semiconductor field effect transistors (MOSFETs, described earlier) for logic functions. The main principle behind CMOS circuits that allows them to implement logic gates is the use of p-type and n-type metal–oxide–semiconductor field-effect transistors to create paths to the output from either the voltage source or ground.

When a *p*-type semiconductor is used here (*p*-MOS), a conducting channel is easily formed by application of a negative gate voltage owing to the position of the Fermi level close to the valence band. This results in a sharp increase in conductance even at small gate voltages. Similarly one can imagine fabricating an *n*-MOS and obtaining a FET which switches (sharp increase in conductance) at small positive gate voltages. The correct combination of these elements can result in the desired logic circuit.

2.2.2. Molecular Field Effect Transistor

The molecular realization of a FET can be best explained using the example of a Carbon Nanotube (CNT). CNTs are one of the ideal candidates for the fabrication of molecular FETs. Carbon nanotubes, long, thin cylinders of carbon, were discovered in 1991 by S. Iijima. These are large macromolecules that are unique for their size, shape, and remarkable physical properties. They can be thought of as a sheet of graphite (a hexagonal lattice of carbon) rolled into a cylinder. These intriguing structures have sparked much excitement in the recent years and a large amount of research has been dedicated to their understanding. What makes it so difficult is that nanotubes have a very broad range of electronic, thermal, and structural properties that change depending on the different kinds of nanotube (defined by its diameter, length, and chirality, or twist).Nanotubes form different types, which can be described by the chiral vector (n, m), where n and m are integers of the vector equation $C_h = na1 + ma2$. The values of n and m determine the chirality, or "twist" of the nanotube. The chirality in turn affects the conductance of the nanotube, its density, its lattice structure, and other properties. Depending on the chirality of the tube, it is either semiconducting (presence of a band gap) or metallic (absence of a band gap). This property of CNTs stems from the electronic structure of graphene. In the energy dispersion of 2D graphite or graphene sheet, the energy bands cross the Fermi-level (E=0) exclusively at the K-point of the Brillouin zone of graphite. The periodic boundary conditions around the circumference of a nanotube require that the component of the momentum along the circumference [18], $k_\perp$, is quantized: $C_h k_\perp = 2\pi\nu$ where ν is a non-zero integer. In a (9,0) tube,

the K-point is an allowed wave-vector of the nanotube i.e., there exists allowed energy levels at the Fermi level, this nanotube shows metallic behavior. In a (10,0) tube. The K-point of graphite is no longer an allowed wave-vector of the nanotube, therefore there exist no allowed states at the Fermi level. This gap of unallowed states form the bandgap of a semiconducting nanotube. This can be clearly seen by observing the density of states as shown in figure 9.

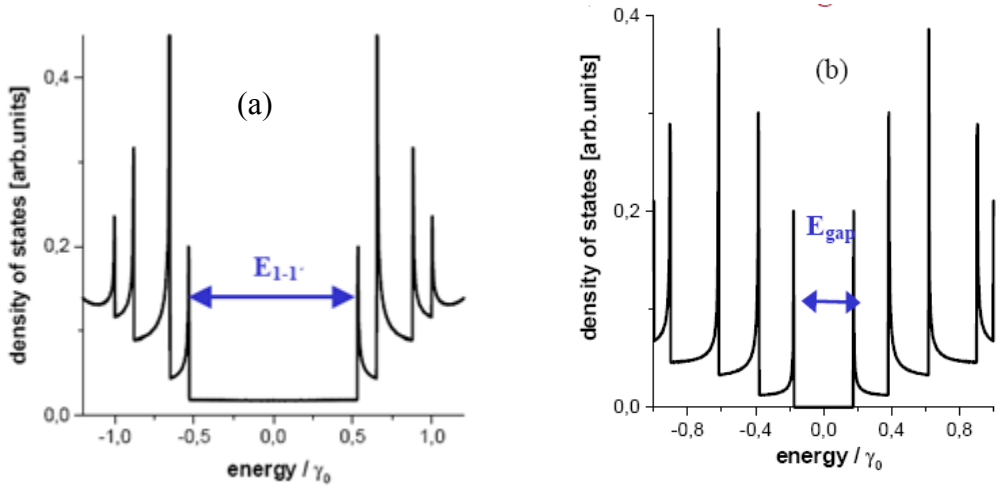


Figure 9 Density of states in a (a) metallic (15,0) tube (b) Semiconducting (14,0) carbon nanotube

As a thumb rule a CNT is metallic if (n-m)=3K where K is an integer, otherwise its semiconducting. Consequently, when tubes are formed with random values of n and m, statistically two-thirds of nanotubes are semi-conducting, while the other third are metallic.

Owing to the large size (compared to other molecules), the fabrication of CNT based FETs is possible using the state of the art technologies used for conventional FETs. Most commonly one uses the bottom gated configuration of a CNTFET. Here the CNTs are deposited on an insulating layer over a conducting substrate which are subsequently contacted with source and drain electrodes. The conducting substrate forms the gate electrode in this case and typically degenerately doped silicon is used for this purpose. However in order to obtain high performance CNTFETs different architectures have been studied. It has been observed that top-gated or wrap-around gated CNTFETs are the most promising because they allow local gate biasing at low voltage, possible high speed switching due to efficient gate coupling, and high density of integration.

This brings us to the concept of the Schottky barrier at the contact-semiconductor interface. In a CNTFET it is important to understand the phenomena occurring at the CNT-Metal interface at the source-drain contacts. In a conventional FET the source and drain contacts are made by degenerately doping the semiconductor. The metal is then evaporated on to these regions there by establishing a smooth Ohmic contact to the doped region. In contrast the metal is directly evaporated on to the CNT causing an abrupt metal semiconductor interface. A Schottky barrier is a potential barrier formed at a metal-semiconductor junction which has rectifying characteristics, suitable for use as a diode. The largest differences between a Schottky barrier and a p-n junction are its typically lower junction voltage, and decreased (almost nonexistent) depletion width in the metal.

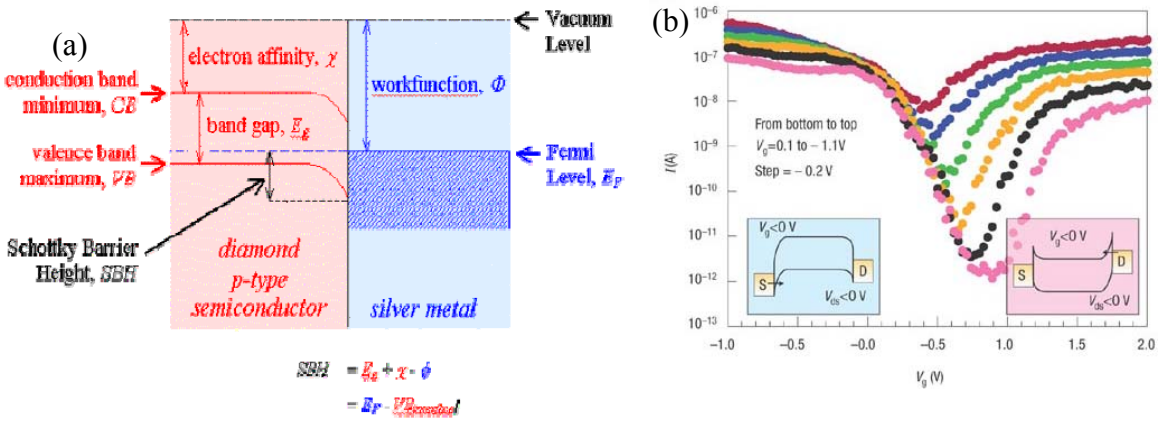


Fig 10 (a) Schematic representation of a Schottky barrier formation. (b) Ambipolar transfer haracteristics (current versus gate voltage). Left inset: schematic of the band structure of a Schottky barrier semiconducting CNT in a FET under negative gate bias. Holes are injected from the source (S). Right inset: under positive gate bias electrons areinjected from the drain (D)

This barrier formation (as illustrated in figure 10 (a)) in a conventional bulk semiconductor occurs as a result of the Fermi level pinning. When the periodic structure of a crystal lattice is terminated at a surface, electronic states particular to the surface are created. These are states that have no equivalent in the band structure of the bulk crystal. Surface-specific states can be true surface states with wave functions which are peaked near the surface plane and which decay in amplitude away from the surface, both toward vacuum and toward the bulk crystal. Surface-specific states can also be surface resonant states that have enhanced amplitudes at the surface but are coupled to bulk states. Of course, the distribution of surface-specific states depends on the atomic structure of the surface, and conversely, the atomic structure of the surface is determined more or less as a result of the minimization of the surface energy, to which the surface-specific

states are a major contribution. Surface-specific states are present at the surfaces of all matters. On metallic surfaces, they are known to lead to a surface dipole which contributes to the work function of the metal surface. On semiconductors, the presence of surface states in the band gap is known to "pin" the Fermi level position of the semiconductor. Pinning does not happen on every semiconductor surface, however, because surface states are not positioned inside the band gap of some semiconductor surfaces, such as the non-polar (110) surfaces of III-V semiconductors. So, on some cleaved non-polar surfaces, there is little band bending. In a CNTs however, the mechanism of formation of the barrier is slightly different. The different work functions of the metal and the CNT lead to transfer of charge at their interface. The resulting interface dipole produces an energy barrier, the so-called Schottky barrier. The alignment of the Fermi levels of the metal and CNT, and therefore the Schottky barrier height, depend on their respective work functions (Φ), the CNT bandgap and the details of chemical bonding at the interface.

CNT-FETs operate as unconventional Schottky barrier transistors, in which switching occurs primarily by modulation of the contact resistance rather than the channel conductance [19]. The gate induces an electric field at the contact, which controls the width of the barrier and hence the current. A sharper contact leads to focusing of the electrical field, allowing operation at lower gate voltages.

Schottky barriers on CNTs can be very useful to fabricate complementary CNTFETs and hence logic devices using CNTs. By careful selection of the contact metals one can either for a *p*-type or *n*-type CNTFET. There are two Schottky barriers in a FET; one at the source and another at the drain as shown schematically in the insets of figure 10 (b). As long as one of the barriers is much higher than the other, the FET operates as a unipolar device; that is, it transports one type of carrier: electrons, or holes. For example, a high work function metal such as Pd (5 eV) could be used to form a nearly barrierless contact for holes (valence band close to the metal Fermi level, E_F), that is to optimize a p-type CNTFET operation, but electron injection at the other end would then experience the maximum barrier. Correspondingly, a low work-function metal, for example, Al (4 eV), will optimize electron transport, but will inhibit hole transport [20]. Changes in work function, affect the Schottky barrier and hence the device characteristics (figure 10 (b)).

2.2.3. Conventional Field Effect Transistor Logic

As explained earlier complementary transistors can be used to perform logical computing. Logic is performed using a binary code which consists of two states 0 and 1. These states are read from the transistors by operating them either in the conductive state or insulating state by

applying the appropriate gate voltage. The logic is performed using circuits called gates which are nothing but the arrangement of the transistors in a circuit that results in the appropriate logic output. The logical operations of AND, OR, XOR, NAND, NOR etc. can be thus performed. A whole computer can be assembled using just NAND gates. Shown below is the fabrication and working of a NOT (inverter) gate.

An inverter circuit outputs a voltage representing the opposite logic-level to its input. Inverters can be constructed using a single NMOS transistor or a single PMOS transistor coupled in series. The typical transfer characteristics of such a device shows a non conductive state at input gate voltages between 0V to 1 V which can be used as logic 0 and a conductive state at 3.5V to 5 V which can be used as logic 1. Thus in such an inverter gate application of 3.5-5 V input would give a 0-1V output and vice versa.

2.2.4. CNT Field Effect Transistor Logic

CNTFET logic analogous to the conventional case would require complementary CNTFETs forming a circuit that yields the required output. One successful attempt to achieve this using CNTs was by local electrical manipulation of the CNTs [21]. A NOT gate fabricated by using *p* and *n* type CNTFETs connected similar to the conventional case described above gives out a logic 0 between 0V and -1V and a logic 1 between -4V and -5V. This local electrical manipulation involved conversion of a p-type FET into n-type by applying a high local gate voltage combined with a large source-drain bias for certain duration.

2.2.5. Ring Oscillators using CNTs

A ring oscillator is a device composed of an odd number of NOT gates whose output oscillates between two voltage levels, representing true and false. The NOT gates, or inverters, are attached in a chain; the output of the last inverter is fed back into the first. Ring oscillators are often used as prototype circuits to test new semiconductor processes, because they are so simple and therefore very easy to design. They also allow running the gates of the new process at optimal speed, which is ideal to optimize the design parameters and layout rules for the new process. In such cases, usually one or a few of the gate outputs are connected to buffers, which are then routed to output pads of the integrated circuits and to external equipment like counters and oscilloscopes. While the single gates operate at very high frequencies (e.g. a few picoseconds of delay), the resulting ring oscillator output frequency is essentially divided by the number of gates in the circuit and therefore accessible to external equipment.

Using the same technique described above to obtain logic gates or by using different contacts one can fabricate ring oscillators using CNTs based inverters. The output of each inverter is the input of the next. Returning the output of the third inverter to the first causes all the inverters to sequentially change logic state, resulting in a three-stage ring oscillator [18, 21].

2.2.5. Graphene based FETs

Considered thermodynamically unstable until recent experimental demonstrations [22] , graphene is the most recent endeavor for the application of carbon nanostructures in conventional electronics. Herein all the carbon atoms are located on the surface and are densely packed in a hexagonal configuration. It is essentially a single layer stripped out of the layered structure of graphite. The two dimensional (2D) structure of this material gives it unique advantages. The high mobility of charge carriers in graphene even at high electric fields renders it ballistically conducting at room temperature. This reduces the switching time of transistors manifold and could potentially be used towards THz transistors.

Electrical contacts to carbon nanotubes typically exhibit high resistance, posing a serious obstacle to their application in electronic devices which is overcome by graphene. The high resistances of CNT based devices imply large RC time constants which translate as low switching speeds. Another distinct advantage of graphene over CNTs lies in its compatibility with existing top down approaches of silicon based technology. The foreseen creation of large area graphene sheets on a silicon surface could lead to the revolution of electronic circuitry and the advent of devices completely carved out of graphene.

Graphene however, being a semimetal (with its bands coinciding at the K points of the reciprocal lattice), result in FETs that show pretty low ratios of I_{on}/I_{off} and also the absence of a gap means that the transistor cannot be turned completely off. To remedy this researchers have used state of the art electron beam lithography and etching techniques to open up a gap in graphene by introducing confinement in 2D graphene. This has been achieved by fabricating upto 20 nm wide graphene ribbons. The gap induced was not large enough to see a significant effect at room temperature. However, when the temperature is sufficiently lowered, the confinement gap starts to impede carrier injection and the device shows a clear on/off ratio as a normal semiconductor.

2.3 Single Electron Transistors

These devices are the ultimate transistors in terms of miniaturization as they function on the principle of a coulomb blockade. Usually electrons move continuously in the common transistors, but as the size of the system goes down to nanoscale (for example, the size of metal atoms can be several nm, and the size of semi-conductive particles can be several tens nm), the energy of the system is quantized, that is, the process of charging and discharging is discontinuous. Thus it requires extra energy for the electron to move into the system which is the repelling energy of the previous electron to the next electron. For a tiny system, the capacitance is very small, thus this energy required can be very high, and the electrons cannot move simultaneously, but must pass through one by one.

A SET is essentially a three terminal device comprising of an island of electrons (For example: small island of a 2DEG system) separated from metal electrodes by an insulator. The source and drain contacts allow one to drive electrons from an external circuit through the island and the gate electrode is used for additional electric field confinement or in other words to modulate the SET. (Details about coulomb blockade and SETs will be dealt in the quantum transport lesson)

Because of its small size, low energy consumption and high sensitivity, SET has found many applications in many areas, such as for single electron memories and high sensitivity electometers. What's most exciting is the potential to fabricate them in large scale and use them as common units in modern computer and electronic industry.

2.3.1. Conventional Single Electron Transistor

A schematic of one kind of SET is shown in **figure** . It consists of a semiconductor, in this case GaAs, separated from metal electrodes by an insulator, in this case AlGaAs. The AlGaAs is doped with Si, which donates electrons. These fall into the GaAs, because their energy is lower in the latter material. The resulting positive charge on the Si atoms creates a potential that holds the electrons at the GaAs/AlGaAs interface, creating a two dimensional electron gas (2DEG). The source and drain contacts allow one to drive electrons from an external circuit through the 2DEG. The 2DEG is confined perpendicular to the GaAs/AlGaAs interface, and the confinement in the other two directions is accomplished with electric fields imposed by very small confinement electrodes. A negative voltage on these electrodes creates a potential which repels electrons from underneath the confinement electrodes and creates potential barriers under the constrictions.. However, the voltage on an additional electrode, the gate, is varied to adjust the potential of the electrons confined in the potential well.

The region surrounded by electrodes in this case was around a few hundred nanometers in diameter. However, the island of electrons confined in it is considerably smaller. It is estimated that these SETs have about 50 electrons confined to a island of about 100 nm in diameter. When the voltage on the gate electrode is increased, the potential minimum, in which the electrons are trapped, becomes deeper. This causes the number of trapped electrons to increase. However, unlike a conventional transistor, in which the charge increases continuously, the charge in the trap increases in discrete steps, and this is reflected in the conductance between source and drain. It can be observed that the conductance increases and decreases by several orders of magnitude almost periodically in Vg.

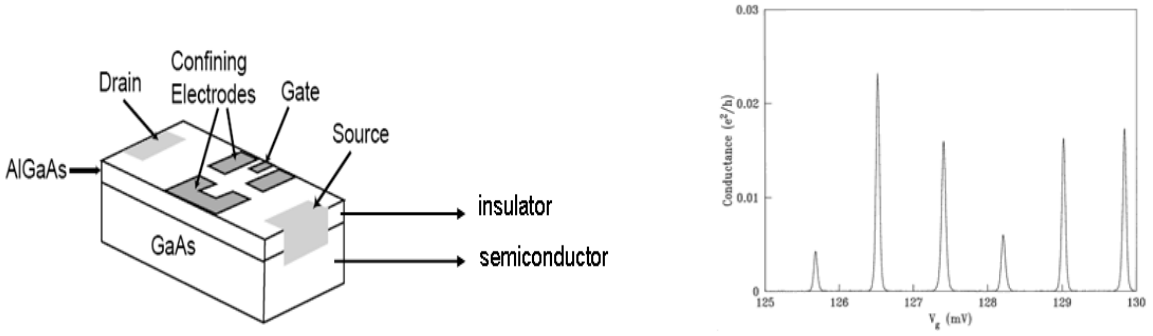


Figure 11 (a) Components of a conventional SET (b) Conductance peaks observed due to the tunneling of electrons through the island.

2.3.2 Molecular Single Electron Transistors

Earlier it was shown how a single molecule (or a few molecules) can function as a diode. If a third electrode (a gate) is included in to the device setup, (for example, by depositing a nanogap onto a gate which is isolated from the device by a thin insulator) this essentially forms a transistor. If a molecule is only weakly coupled to the source and drain, we have a molecular single electron transistor.

One successful approach to fabricate a molecular SET shall be described in the following. A planar gate electrode made of aluminium metal covered with aluminium oxide was prepared on a chip of oxidized silicon. A shadow mask used to deposit the gold lead electrodes was defined on top of the gate by standard electron-beam lithography. The chip was then introduced into a vacuum chamber immersed in liquid helium. First, two gold electrodes were deposited through a shadow mask by condensing gold vapor on the substrate held at 4.2 K. By using an oblique evaporation angle ogether with in situ conductance measurements, the tunnelling gap between gold electrodes was fine-tuned to a few nanometers. Second, a submonolayer (,1%) of organic

molecules was deposited on the electrodes by quench condensation. The sample was annealed at low temperature (below 70 K) allowing thermally activated motion of the organic molecules, while monitoring the nanogap conductance at a source–drain bias of 400mV. The step wise change in conductance changed, indicated the trapping event of a single molecule in the nanogap. The temperature was cooled down again to arrest the thermally activated motion and study the transistor action of the trapped molecule.

In a molecular SET the HOMO and LUMO of the molecule correspond to the N^{th} and $(N+1)^{th}$ state of the conventional electron island. Electrons can only from the source or drain if the potential of the electrode aligns with (or exceeds) the molecular level. Below these potentials, no electrons can flow which is nothing but the Coulomb blockade. By changing the gate voltage (Vg) of the SET with a single molecule in the nanogap in small steps while measuring the source–drain current–voltage characteristics (I–V) at each step, eight different transmitting (open) states of the SET could be probed. This is summarized in a coulomb diamond plot, where the dark diamonds correspond to zero-current regions, where the low bias transport is blocked [23].

Room temperature single molecule transistors using Carbon Nanotubes: Carbon nanotubes when carefully modified can be used as single electron transistors which work at room temperature. This device was fabricated by first depositing CNT bundles on an insulating Silicon Dioxide susbtrate, which were then contacted using electron beam lithography to provide the source and drain electrodes. In order to use this device as a SET one has to locally modify the tubes. This can be achieved by depositing V_2O_5 nanowires of 10 nm diameters across the CNT bundles and the subsequent evaporation of Silicon Monoxide which acts as protective layer against acid attach which is used to remove the nanowires. This leaves a ~10 nm gap in the SiO layer on the CNT bundles. The open section of the tube was then modified using a 2 second pulse of Oxygen plasma which modified the tube creating a tunneling barrier. This device was studied at room temperature and the differential conductance (dI/dV) is plotted against bias voltage revealed that the coulomb blockade gap was around 41 meV. [24]

Thus it can be seen that electronic devices based on molecules is growing field with enormous potential to be the future of conventional electronics. The above described devices are a snapshot of a myriad of efforts into using molecules for various applications thus transcending the barrier to the Moore´s law posed by the fundamental and technological limits of present day silicon technology.

3. References

[1] Aviram, A., Ratner, M. A. (1974) Chem. Phys. Lett. 29, 277–283.

[2] M. Zharnikov et al., Phys. Chem. Chem. Phys. 2000, 2, 3359-3362

[3] J.C.Love et al, J.Am.Chem.Soc. 2003, 125, 25097-2609

[4] L.Patrone et al, Chem. Phys. 2002,281,325-332

[5] P. Morf et al, Langmuir 2006, 22, 658-663

[6] J.Chen et al, Chem. Phys. Lett. 1999,313, 741-748

[7] A. Ulman, Chem. Rev. 1996, 96, 1533-1554

[8] J.Moreland et al, J. Appl.Physics 1985, 58, 3888-3895

[9] J.M.V. Ruitenbeek et al., Rev. Sci. Instrumen. 67 (1996), 108

[10] R.Sordan et al, Appl. Phys. Lett. 87, 013106 (2005)

[11] Mark A. Reed, Nature Materials **3**, 286 - 287 (2004)

[12] B. Xu et al., Science 301(2003), 1221.

[13] D.I.Gittins et al, Nature 2000, 408, 67-69

[14] Y.Yasutake et al, Nano Lett. 2005, 5, 1057-1060

[15] W. Wang et al, J. Phys. Chem. B 108 (2004), 18398.

[16] A. Blum et al, Nature Mater. 4 (2005), 167.

[17] Guo et al, Science 311 (2006), 356

[18] Avouris et al, Nature Nanotech. **2**, 605, (2007)

[19] Heinze et al, Phys. Rev. Lett. **89**, 10 (2000).

[20] Javey et al, IEDM Technical Digest 741, (2003)

[21] Javey etal, Nano Lett. **2**, 929, (2002)

[22] Novoselov et al, Science 2004, 306, 666.

[23] S. Kubatkin et al, Nature **425**,698 (2003)

[24] J. B. Cui Nano Letters 2,117(2002)