ELECTRICAL PROPERTIES OF JUNCTIONS BETWEEN ALUMINUIM AND POLY[3-(2'-OCTYLOXY-5'-(1'''-OXOOCTYL)PHENYL)THIOPHENE]

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by

Bekele Homa

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Addis Ababa

Declaration

I declare that the thesis is my original work, has not been presented for a degree in any other University and that all sources of material used for the thesis have been duly acknowledged.

Name: Bekele Homa

Signature:

Place and date of submission: Addis Ababa University
Department of Physics
June 2003

This thesis has been submitted for examination with my approval as University advisor.

Name: Dr. Bantikassegn Workalemahu

Signature:

Date:

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Finally, my gratitude goes to my brother Gadissa Homa and my friends to Adane Samuel, Ashenafi Feye and Jicksa Mulisa for we had good time together during our stay

Dedication

To my sister

Brihane Homa

Table Of Content

ABSTRACT

In this thesis, the property of the junction between aluminium and neutral conjugated polymer is studied. The conjugated polymer used is poly[3-(2'-octyloxy-5'-(1'''-oxooctyl)phenyl)thiophene] which is the derivative of polythiophene having 8-carbon atoms alkyl side chain which makes it different from other thiophene derivatives.

The techniques employed are optical absorption spectrum, I-V characterization and impedance spectroscopy study. Optical spectroscopy study showed the optical band gap of the polymer is 2.03eV indicating the polymer is in the range of conventional inorganic semiconductor. Based on this result the theoretical background in studying the property of junction between aluminium and the polymer is that of conventional inorganic semiconductors.

The I-V characteristics of Al/poly[3-(2'-octyloxy-5'-(1'''-oxooctyl)phenyl)thiophene]/ITO structure showed non-ohmic, non-rectifying and nearly symmetrical curves. The complex impedance analysis exhibited a semicircle whose diameter depends on the magnitude of the applied bias voltage; the diameters are small for larger bias voltages and increases for small intermediate bias voltages. This result is consistent with the I-V characteristics. Therefore, the junction between aluminum and the polymer forms no Schottky barrier.

1. Introduction

Polymers are defined chemically as long-chain molecules of very high molecular weight, often measured in hundreds of thousands of g/mol. For this reasons, the term macromolecule is frequently used when referring to the polymeric material [1]. Organic polymers were known to be typically insulators and they were usually considered as uninteresting from point of view of electronic properties [2]. However, in 1977 it was reported that organic polymer, polyacetylene, could be rendered conducting by doping with an appropriate molecule [3]. The new group of material arising from this discovery adopted the name conducting polymer.

Conducting polymers are usually called conjugated polymers, as their conducting behaviors arise from the strict alternation of single bond and double bonds along the chain. Conducting polymers immediately launched worldwide researches after their inception. The early effects were mainly of basic nature, often theoretical studies. Later on experimental studies and device fabrications become dominant. Most organic polymers are intrinsically insulators. But conducting polymers can be made to conduct with conductivity varying from insulating through semiconductor to metallic by the process of doping.

In polymers, just as in crystals, the interaction of polymer unit cell with all its neighbors leads to the formation of electronic band. The highest occupied electron levels constitute the valance band (VB) and the lowest unoccupied level, the conduction band (CB). The width of the forbidden gap, between the conduction band and valance band, determines the intrinsic electrical properties of the materials. For all common organic polymers, the band gap is above 1.5eV [4]. Therefore, these materials are considered as large band gap semiconductors.

The important difference between organic and inorganic materials is that organic materials are much softer than inorganic materials. This makes it energetically favorable to localize the charge appearing on the chain up on doping and to have a bound charge, a local distortion or relaxation of lattice. The conduction mechanism of charge carriers is not exactly the same as that of conventional inorganic semiconductor. It follows the conduction mechanism of amorphous semiconductors.

For integration into electronic system, these materials will have to be interfaced to metals or semiconductors. The nature of the junction between conducting polymers, in their undoped and doped forms, and metals is thus as important as that of inorganic semiconductor. Active devices based on junction between conjugated polymers and metals are widely studied [5].

The reason of such intense study on these materials is due to their wide range of application in electrical and optical devices [6]. Now days many research works are devoted to the production of polymer-based optical and electronic devices as light emitting diodes (LED) [7-13], micro actuators or micro mussels [14], photovoltaic devices [15-18], field effect transistor (FET) [19], and many other devices.

With this rate of polymer device inventions and fabrications, electronic computers based on polymers and polymer based integrated circuits, will soon find their place in consumer products where low processing costs will be more important than high speed.

2. Physics of Conjugated Polymers

Recently, organic materials 'conducting polymers' are becoming interesting from the point of view of electronics and optics. There are several reasons why this is so, these are: the low cost of organic materials, flexibility to form thin films and so fourth. However, due to instability, processability, synthesis and design large number of multidisciplinary research activity awaits ahead. To study the special electrical properties of conjugated polymers we need to look at the chemical bonding formed in the polymer chains.

2.1. Hybridization

The process of combining two or more atomic orbitals to create new orbitals called hybrid orbitals is known as hybridization. Two axioms of quantum mechanics namely Heisenberg uncertainty principle and Pauli exclusion principle are the basis for understanding the formation of atomic orbitals. The atomic orbitals of two hydrogen atoms form a molecular orbital (MO) if they are brought close enough so that they overlap. There are two possible ways in which the wave functions of the electrons in both hydrogen atoms superpose. One of these MOs is significantly lower energy than the original atomic orbitals. It is known as a bonding MO. The other orbital, called an antibonding MO is of higher energy than the original atomic orbitals.

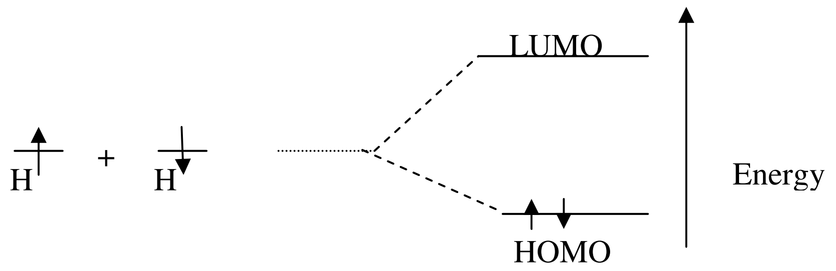


Fig.2.1. *Energy schematics showing the overlap of the 1s atomic orbitals of two H atoms to form a bonding and anti bonding molecular orbitals.*

The bonding MOs that results in geometry of cylindrically symmetrical about a line joining the two nuclei involved is called sigma (σ) orbitals and the bonds formed are called σ-bonds.

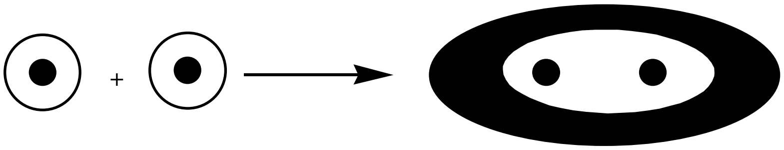


Fig.2.2. *Cylindrically symmetrical σ-bonding of hydrogen molecule*.

Another type of bonding MO and therefore a second type of covalent bond can be formed by the overlap of two atomic 2P orbitals as shown in the figure below.

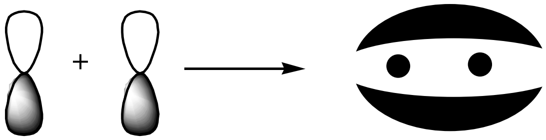


Fig.2.3. *Overlap of two parallel p atomic orbitals to give a bonding π MO*

Hybridization of atomic orbitals is of fundamental importance in understanding the nature of covalent bonds. For instance, if we consider methane, the carbon atom may be realized by mixing the 2s and the three 2p orbitals creating set of four degenerate orbitals referred to as sp^3 hybrid orbitals.

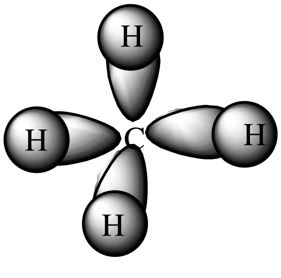


Fig.2.4. *The sp^3 hybridized carbon atoms in methane*.

Each sp^3 orbitals combine with the hydrogen 1s orbitals to form bonding molecular orbitals. The sigma bonds are tetrahedrally oriented from the central carbon atom. Usually hybrid orbitals are known to form sigma bonds. However, double bonded orbital hybridization such as ethylene uses a different pattern of orbitals for bonding. In this case the carbon atoms mix the 2s and two of its 2p orbitals and one of the 2p orbital is leftover in each carbon atom. The sp^2 hybrid orbitals form σ-bond with each hydrogen atoms and the unhybridized 2p orbitals in each carbon atoms overlap by side to form π-bond in addition to the σ-bond formed by hybrid orbitals.

The nature of hybrid orbitals has a significant impact on the structure of the polymers. Polymers having sp^3 hybridization are bound to form σ-bonds only. Consequently, the separation between HOMO (Highest Occupied Molecular Orbitals) or valance band and anti bonding LUMO (Lowest Unoccupied Molecular orbitals) or conduction band is large. On the other hand, sp^2 hybridization having π-bonds in addition to the σ-bonds yields smaller separation between the bonding (π) and anti-bonding (π*) states having smaller E_g.

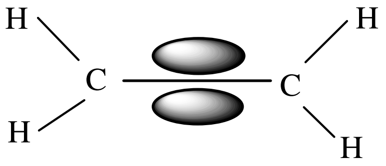


Fig2.5. *Double-bond character of ethylene,* C_2H_4*. All σ-bonds are represented by straight lines. The* p_z *atomic orbitals of C atoms overlap to form bonding molecular π-orbital.*

The class of polymers having π-bonds, by virtue of having a combination of both σ-and π-bonds can be categorized into two forms: those with localized and delocalized electronic states, respectively. The polymers with delocalized electronic configuration are capable of being doped to high electrical conductivity [5].

2.2. Conjugation

Organic molecules that contain double bonds show different electronic properties compared to saturated molecules, which have single bond only. Specially in the case of alternating single bond and double bonds, called conjugation. The chain structure of conjugated polymer has a regular sequence of strictly alternating single and double bonds. The most well studied and prototype example of conjugated polymers is polyacetylene (PA) for its well-established and standard database, though there are other types of polymers that manifest similar electrical properties as polyacetylene.

Polyacetylene is the simplest conjugated polymers. It has different isomers cis and trans of which the latter is found to be well explaining the theoretical background of conducting polymers. Trans polyacetylene has structure as in Fig.2.6.

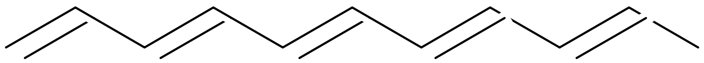


Fig.2.6. *Trans polyacetylene, strict alternation of single and double bonds*

Therefore, $(CH)_x$ is frequently referred to for a better understanding of fundamental properties of conjugated polymers. Because of the strong interchain bonding characteristics of such polymers the π-electrons are delocalized principally along the polymer chain. These systems are therefore electronically one-dimensional. Quasi-one dimensional metals tend to distort spontaneously following Peierl's transition [20-22]. Dimerization or conjugation of polyacetylene can be studied using Peierl's distortion of one-dimensional metals. Polyacetylene is said to be undimerized when all bond lengths along the PA backbone are equal and spare electrons are delocalized over the whole system see Fig.2.7. It becomes dimerized when the electrons are localized to form alternating single and double bonds.

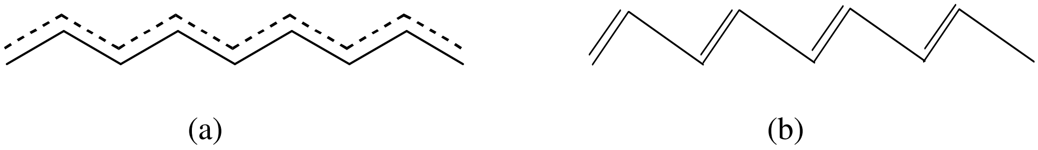


Fig.2.7. *(a) delocalized (b) localized electron in polyacetylene***.**

Undimerized PA is similar to undistorted chain of atoms with lattice constant "a" and dimerized PA is similar to distorted chain of atoms with lattice constant "a". The dispersion relations for both types of PA are shown in Fig.2.8. In PA there is an alternation of single and double bonds. The double bonds are slightly shorter than the single bonds. This difference in the bond lengths distorts the array of the lattice and doubles the elementary cell of one-dimensional crystal from lattice constant "a" to "2a". Doubling of the lattice constant in real space corresponds to reducing first Brillion zone by half in reciprocal space [5]. This introduces discontinuity in the dispersion relation as shown in Fig.2.8(b). Thus, dimerization of the undimerized PA changes the polyacetylene from metallic to non-metallic state.

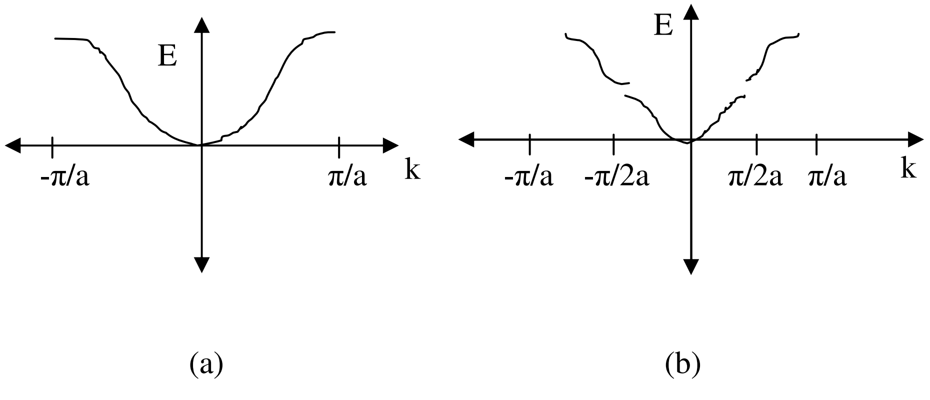


Fig.2.8. *Dispersion relations for (a) undimerized polyacetylene (b) dimerized (localized) polyacetylene*

Several optical studies have been done to calculate the energy gap of dimerized PA to be 1.4eV [5], which is in the region of semiconductors. Since dimerization (distortion) can start from whichever ends of the chain trans PA has two configurations having the same ground states. The existence of such degenerate states will help us in studying elementary excitations in the next chapter.

3. Elementary Excitations

Modern theory of condensed matter is based on the assumption of the existence of stable ground states and of low-lying exited state above it. In most cases the energy of excited states (with respect to the ground state) can be expressed as a sum of elementary excitations like phonons, spin waves (magnons), excitons, and photons [5].

The mechanisms of electrical conduction in inherently conducting polymers are still a matter of controversy. The charge carriers are not electron as in inorganic conductors and semiconductors. However, the concept of elementary excitations, namely soliton, polarons and bipolarons acting as charge carriers has been widely accepted. Therefore, the subsequent discussion will be devoted to those excitations.

3.1. Soliton

The historical emergency of the word soliton is from the solitary wave, a rounded, smooth and well-defined heap of water created by suddenly stopped boat in a narrow cannel and propagating along it without change of form and diminutions in speed [23]. This wave is considered to be the solution to non-linear differential equation depending on special initial condition. Hence soliton.

For instance, in PA we use the word soliton is used for the topological defect in lattice configuration and an electron bound state associated with this defect. We may also use the term kink, misfit or domain wall if only lattice distortion is concerned. Trans PA has two configurations having degenerate ground states called A and B phases respectively as shown in the Fig.3.1.

Fig.3.1. *Degenerate ground states of polyacetylene***.**

The kink is a defect where these two phases have a 'misfit' as schematically shown in Fig.3.2.

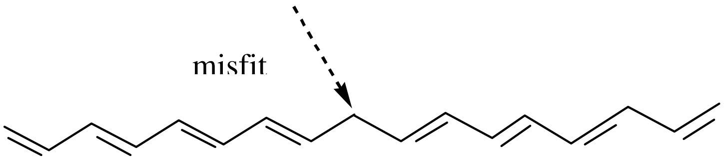


Fig.3.2. *Domain wall (misfit) separating a trans PA chain into phase A and B.*

The misfit or domain wall separates the polymer chain into phase A and phase B, which are termed as domains. To find out the charge and the spin of this defect state we can use extremely dimerized approximation in which all double bonds are doubly occupied with zero resulting spin but the electron at the defect site is in the zero energy, non-bonding state. On the other hand the whole chain is electrically neutral. Therefore, this defect state has zero charge but spin 1/2. Moreover, if we remove this electron or add new one in the non-bonding state, the spin becomes zero but the charge becomes ±e. This is in sharp contradiction with conventional excitations like electrons or holes with spin 1/2 and charge ±e [23]. It was also found that the creation energy of this soliton state 'non-bonding' state is less than the electron and hole energy. This means that the soliton is a more stable excitation and thus should play a more important role [23] in transport mechanism of conducting polymers. At the misfit the atomic orbitals do not 'know' whether they should form bonding (π) or anti bonding (π^*) state. They form non- bonding states in the energy gap and because of the symmetry reasons they form a mid gap state called non-bonding state [5] as shown in Fig.3.3.

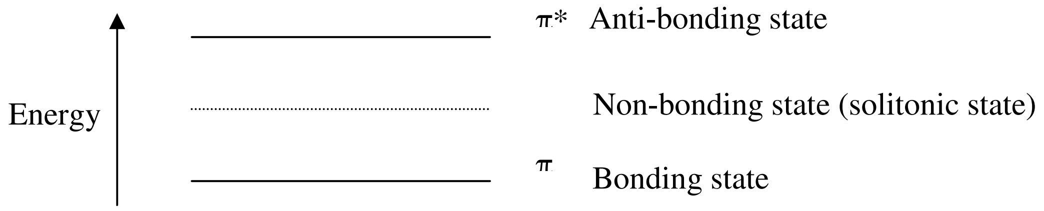


Fig.3.3. *Formation of mid gap state.*

There are two mechanisms of soliton generation. The first one is intrinsically formed soliton during synthesis or dimerization and the second is doping induced soliton. Doping of conjugated polymer is a chemical redox reaction. Up on doping, charge transfer between dopant and polymer takes place. As a result of this the non-bonding state will have three possible solitonic charges, namely, mid-gap states charge +e, 0, -e as shown in Fig.3.4.

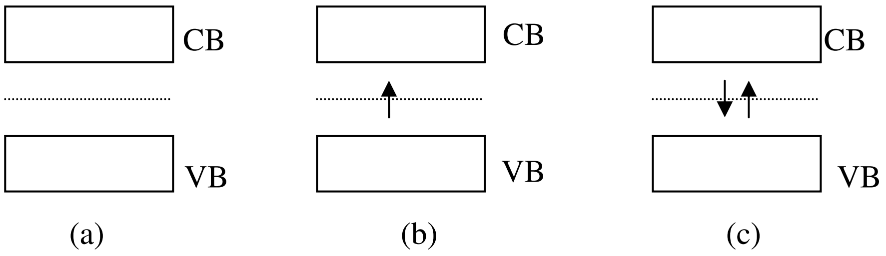


Fig.3.4. *Band diagram of polyacetylene with soliton (a) positive soliton q=+e, s=0, (b) neutral soliton q=0,s=1/2, (c) negative soliton q=-e, s=0.*

From the above discussion it is clear to see that charged solitons do not carry spin and while neutral solitons have spin 1/2. In other words the soliton has spin 1/2 with zero charge if the bound state is singly occupied, and zero with charge ±e if it is doubly occupied or empty. Hence spin charge inversion.

3.2. Polarons and Bipolaron

Solitons are stable in polyacetylene since it has two-fold degenerate ground state. But in other polymers that do not have two-fold degenerate ground state the soliton will move from the lower energy to the higher energy ground state. To exemplify the statement we can consider non-degenerate ground states of polythiophene as depicted in Fig.3.5. The left side of soliton indicated in Fig.3.5 is aromatic and the right one is quinoidal. Breaking conjugation at the misfit leads to a transition from an aromatic to quinoidal state. Thus, the soliton separates high energy and low energy. Contrary to soliton in polyacetylene, solitons in non-degenerate polymers are energetically unstable.

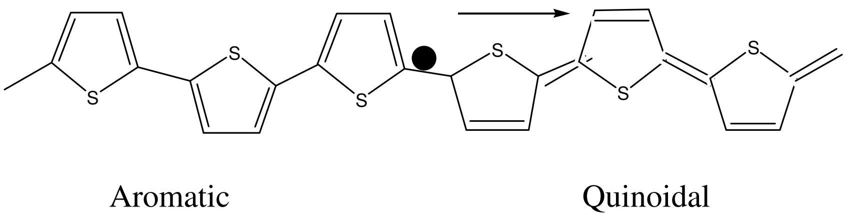


Fig.3.5. *Non-degenerate states of polythiophene. The energy of the aromatic configuration (ground state) is less than the quinoidal (excited) state energy. Hence, the lattice force in the direction of the arrow drives the soliton.*

They move toward the end of the chain there by changing the high energy the high-energy quinoidal rings into low energy aromatic rings. If the defects in non-degenerate ground states polymers are to be stable, bound double defects must be created as in the Fig3.6. This bound double-defect leads to other form of elementary excitation called polaron [5].

Polaron can be viewed as an interacting charged soliton- neutral anti-solitons pair. For instance, PA at higher doping levels, the pairs interact, their radical recombine and the process leads to charged solitons. On more complex organic polymers, which become conducting with suitable doping solitons cannot be created because they lack the degenerate ground state as the case in PA. They could, however, support doubly charged polarons known as bipolarons (see Fig3.7), which have been proposed as the spinless charge carrier in such a system.

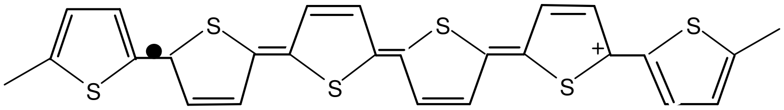


Fig3.6. *Formation of a polaron in polythiophene.*

Polaron has two bound states, which is symmetric with respect to the gap center and can be thought of as the bonding and anti-bonding combinations of the two mid gap states associated with the bound soliton pair that makes up the polaron; in effect the lower state is split off from the bottom of the conduction band. Each of these states accommodates one electron of each spin orientation. Absorption spectrum of different polymers shows the existence of inter band states, which are symmetric with respect to the mid gap energy. This two inter band states come from the two kinks of polarons or bipolarons.

The spin of the charge neutral case is zero, since all states both continuum and localized, are doubly filled. Therefore, the electron and hole polarons each carry 1/2 and the spin charge relation is the conventional one [2].

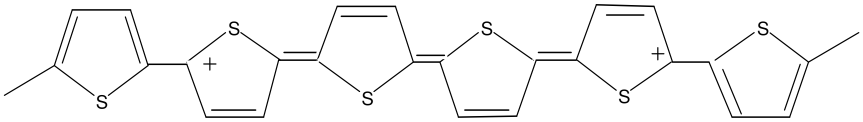


Fig.3. 7. *Bipolaron in polythiophene*

Total energy calculations show that only the electron and the hole polarons are stable. If one adds, for example a second electron to an electron polarons the resulting 'bipolarons' lowers its energy by increasing the soliton-soliton spacing until a free kink or anti-kink pair evolves at large separation thus, up on doping the first injected electron forms a polaron; the second injected electron breaks apart the polaron to form two negatively charged kinks. However, when the precise ground state degeneracy of the polymer is lifted, the resulting confinement of the solitons leads to stable bipolarons [2].

Since a polaron is stable only in the absence of another polarons, the role played by a polaron in trans PA is rather limited. However, kinks can exist only in systems with exact ground state degeneracy. As most conducting polymers posses only near degeneracy, polarons and bipolarons take over the major role played by the kinks.

3.3. Hopping Conduction

When charge carriers are highly localized they move by hopping from site to site being scattered at virtually every step. The motion of the carrier is characterized by the magnitude and the temperature dependence of the mobility [24]. For strongly localized carriers i.e. μ, mobility, is much less than unity and it is temperature dependant as $\mu = \exp(-E / kT)$, where E is activation energy.

Hopping model conductivity emphasizes the molecular character of conduction states, while the band model emphasizes the collective character of conduction states. Molecular crystals fall in an intermediate category in which $\mu \approx 1 cm^2 v^{-1} s^{-1}$ and the temp dependence shows evidence of band a hopping motion.

Carriers may be scattered by transitory symmetries induced by temperature; thus crystal phonon scatters the carrier. The scattering of the carrier by thermal vibrations is illustrated schematically as in Fig.3.8 where a phonon is shown as a peak (on the energy surface) that a moving electron cannot surmount. These phonon-carrier interactions can involve either acoustic or optical phonon. Each scattering process can be treated as either in the first order, i.e. a one-phonon process or as a higher order event in which more then one phonon is involved simultaneously [24].

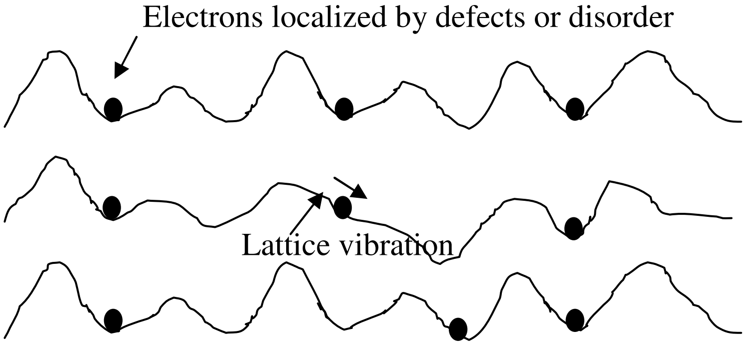


Fig3.8. *Schematics of phonon assisted hopping.*

Since hopping conductivity is assisted by phonon, it freezes out as temperature falls to zero. In view of this hopping depends strongly on temperature if the electronic states are strongly localized. If localization is less strong, electron can jump to sites for which the activation energy is smaller but which can reside further away i.e. conduction occurs by variable-range-hopping hopping [3]. As the temperature is decreased fewer states fall within the allowed energy range and the average hopping distance increases. As a result the hopping probability and thus, conductivity decreases. The temperature dependence of the variable range hopping conductivity is given by [3]

$$\sigma = \sigma_2 \exp\left[-\left(\frac{T_3}{T}\right)^{\frac{1}{d+1}}\right]$$

Where d indicates the dimensionality, and $T_3 \propto [a^d N(E_F)]^{-1}$ where N(E_F) is the density of states and 'a' denotes the localization length, the prefactor $\sigma_2(T)$ is more slowly varying than the exponential.

4. Metal-Semiconductor Contacts

The contact between metal and semiconductor is well studied based on the surface parameter of metal and semiconductor called work function. Work function of metal ($e\phi_m$) or semiconductor ($e\phi_s$) is the energy required to raise an electron from the Fermi level to a state of rest out side the surface of the metal or semiconductor (the so called vacuum level). Other parameter to be used is electron affinity of the semiconductor, the energy required to raise an electron from the bottom of the conduction band to the vacuum level. Fig.4.1 shows the schematics of metal with higher work functions and n-type semiconductor before contact.

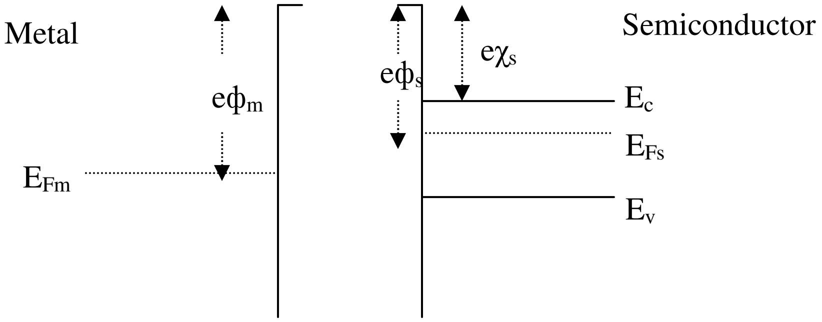


Fig.4.1. *Ideal energy band diagram of metal and n-type semiconductor whose work function is less than that of metal ($\phi_m > \phi_s$).*

The metal and the semiconductor are assumed to be neutral before contact. After contact is made the ideal thermal equilibrium metal semiconductor energy band diagram is shown in Fig.4.2. At equilibrium the two Fermi levels are forced to coincide. In order for the Fermi level to become a constant through the system in thermal equilibrium, electrons from the semiconductor flow into the lower energy state in the metal [25,26]. Consequently, positively charged donor atoms remain in the semiconductor creating space charge region as shown in Fig.4.4. The uncompensated donor atoms occupy a layer of appreciable thickness, w.

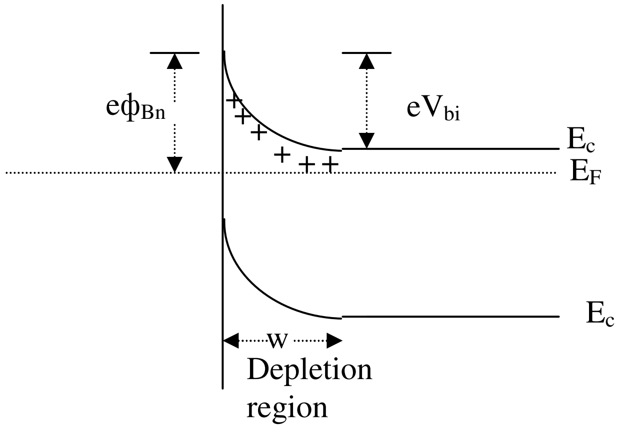


Fig. 4.2. *Ideal energy band diagram of metal and n-type semiconductor junction for* $\phi_m > \phi_s$.

Clearly electric field is created in the depletion region pointing from right to left see Fig.4.2. Under zero bias electrons will not flow from the bulk semiconductor in to the metal because of the barrier created or built in potential, eV_{bi}, between conduction band at the junction and at the bulk. This barrier is called Schottky barrier.

If positive voltage is applied to the semiconductor relative to the metal, the voltage will be added to the built in potential and hence the barrier height increases and the area of depletion region widens. Therefore, there will be no current flow across the junction. If the metal is connected to higher voltage, the applied external electric field will decrease the barrier height and depletion region will be narrower. Hence there exists current flow.

The above description applies to an n- type semiconductor with work function ϕ_s less than the work function of the metal ϕ_m and it is seen that such contact behaves as a rectifier. If a similar argument is developed for the case of when ϕ_s is greater than ϕ_m one obtains a band diagram as shown in the Fig.4.3(c). Obviously, if such a contact is biased so that electrons flow from the semiconductor to the metal, they encounter no barrier. If it is biased so that electrons flow in the reverse direction, the comparatively high concentration of electrons in the region where the semiconductor bands are bent down wards (usually referred to as accumulation region) behaves like a cathode, which is easily capable of providing a copious supply of electrons. The current is then determined by the resistance of the bulk semiconductor rather than by the properties of the junction [27].

In p-type semiconductor for which ϕ_m exceeds ϕ_s, we obtain the band diagram as shown in Fig.4.3(b), which also represents an ohmic contact. The case of a p-type semiconductor for which ϕ_s exceeds ϕ_m is shown in Fig.4.3(a). Since holes have difficulty in underneath [22], a barrier one sees that Fig.4.3(a) is the p-type analogue of Fig.4.2 and gives rise to rectification.

The contact between p-type semiconductors for which ϕ_m exceeds ϕ_s and n-type semiconductors for which ϕ_m is less than ϕ_s are ohmic. Therefore, they are very uncommon in practice. The majority of metal-semiconductor combinations form rectifying contacts.

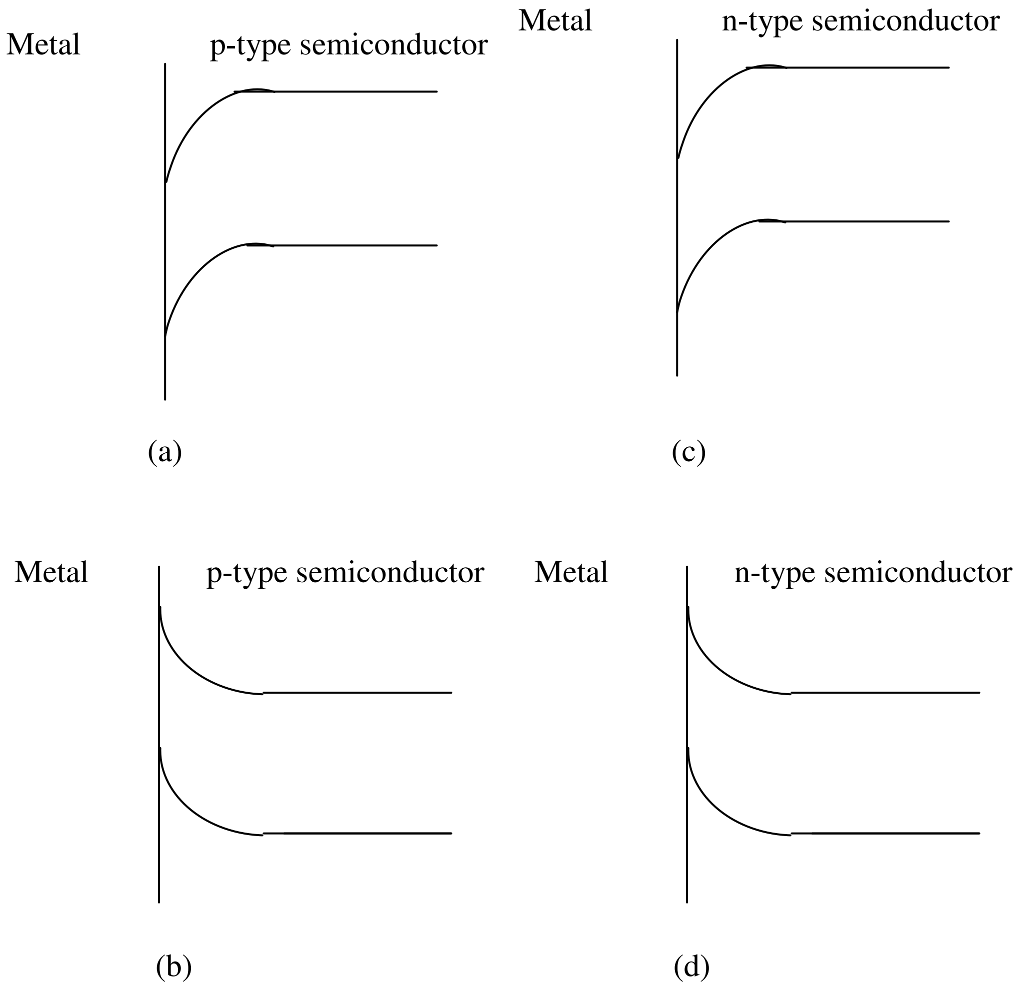


Fig.4.3. *(a) metal-p-type semiconductor contact for* $\phi_m<\phi_s$, *(b) metal-p-type semiconductor for* $\phi_m>\phi_s$, *(c) metal-n-type semiconductor contact* $\phi_m<\phi_s$ *and (d) metal-n-type semiconductor for* $\phi_m>\phi_s$.

4.1. Current-voltage characteristics

There are various ways in which electrons can be transported across metal-semiconductor junction under forward bias. The schematics for n-type semiconductor is as shown in the Fig.4.4. These are:

a) Emission of electrons from the semiconductor over the top of the barrier into the metal.

b) Quantum mechanical tunneling through the barrier.

c) Recombination in the space charge region.

d) Recombination in the neutral region (hole injection).

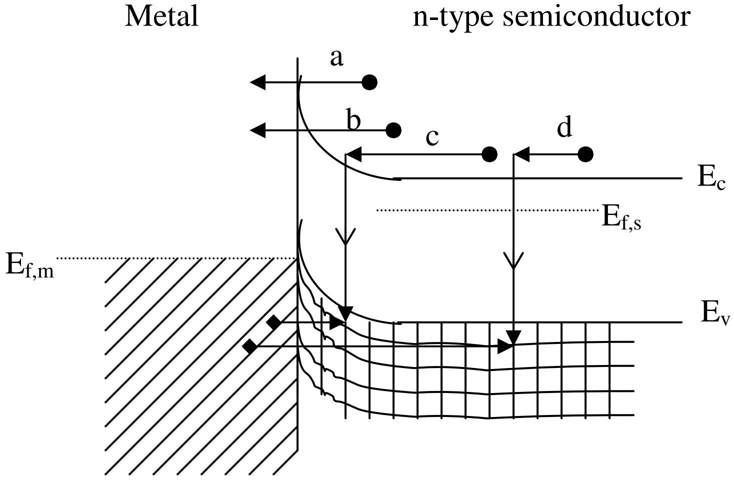


Fig.4.4 *Basic transport processes under forward bias Schotkky barrier diode***.**

Out of the four mechanisms emission over the barrier is the dominant process [27]. Therefore, the well known thermo-ionic emission equation governs the current voltage characteristics.

$$J = J_s[\exp(\frac{qV}{nkT}) - 1], \qquad 4.1$$

where $$J_s = A^{**}T^2 \exp(-\frac{q\phi_{bi}}{kT}). \qquad 4.2$$

Where J is the total current density, q is the charge of an electron, V is the applied forward voltage, k is Boltzmann's constant, T is absolute temperature, n is diode ideality factor, ϕ_{bi} is barrier height and A** is modified Rechardson constant which expresses the number of electron at the semiconductor metal interface that may be injected into the metal. Modified

Rechardson constant also takes into account the effective density of states in the conduction band. For organic semiconductor Schottky diodes the modified Rechardson constants is assumed to be that of free electron i.e. A** =120A/cm^{2}K^2.

The thermionic emission equation for J-V can be studied under three different conditions of $J_{s.}$ These are:

Case (1) if J>>J_s the contact will effectively block current flow for reverse bias voltage and will display an exponentially increasing current for forward bias. Thus, the diode rectifies.

Case (2) if J<<J_s, the junction readily pass current for both signs of the applied voltage. Hence ohmic contact.

Case (3) if $J \cong J_s$, i.e. if J and J_s are comparable, the J-V curve is neither rectifying nor ohmic but symmetric.

4.2. Junction Capacitance

When a reverse voltage is applied to the junction, the electric field will uncover the dopants and increase the space charge region. Depletion region depends on the reverse voltage as

$$w = \left[2\varepsilon_s \frac{(V_{bi} + V_R)}{eN_d} \right]^{1/2} \qquad 4.\ 3$$

If the reverse bias is increased by dV_R, the space charge will increase by dQ. For uniformly doped semiconductor dQ is given by

$$dQ = eN_d dw \qquad 4.4$$

The differential charge dQ is in unit of Coul/cm^2 so that the capacitance C is in unit of Farad/cm^2 or capacitance per unit area.

$$C = \frac{dQ}{dV_R} = eN_d \frac{dw}{dV_R} \qquad 4.5$$

Up on substituting w from equation 4 and differentiating we get the capacitance for Schottky diode as

$$C \approx \left\{ \frac{e\varepsilon_s N_d}{2(V_{bi} + V_R)} \right\}^{\frac{1}{2}} \qquad 4.\ 6$$

Equation 6 can be rewritten as

$$\left(\frac{1}{C}\right)^2 \approx \frac{2(V_{bi} + V_R)}{e\varepsilon_s N_d}$$

Where ε_s is permitivity of semiconductor, N_d is dopant concentration, V_R is reverse bias voltage, V_{bi} is built in potential.

5. Impedance Spectroscopy

Impedance spectroscopy is a relatively new and powerful method of characterizing many of the electrical properties of materials and their interface with electronically conducting electrode.

5.1. Impedance and related functions

If monochromatic signal $v(t)=v_m\sin(\omega t)$, involving the single frequency $\upsilon=\omega/2\pi$ is applied to a certain circuit system and the resulting steady state current $i(t)=i_m\sin(\omega t+\theta)$ measured. There exists capacitor or inductor that responds to the stimulus in such away that the phase difference between the voltage and the current is θ. The phase difference is zero for purely resistive behavior. Thus impedance can be define as

$$Z(\omega)=\frac{v(t)}{i(t)}$$

its magnitude of modulus is given by $\left|Z(\omega)\right|=\frac{v_m}{i_m}$ and its phase angle is $\theta(\omega)$.

Impedance is the more general concept than resistance because it takes phase differences into account and it became a fundamental and essential concept in physics and engineering. Impedance can be described as a planar vector in a right hand orthogonal system of axes can be expressed by the vector sum of the components Z' and Z'' along the axes, i.e. by complex number Z= Z' + jZ''. The imaginary number $j=\sqrt{-1}$. The real part, Z', is in the direction of the real axis X, and the imaginary part, Z'', is along the Y-axis. An impedance Z(ω)= Z'+jZ'' is such a vector quantity and may be plotted either in rectangular or polar coordinates as shown in Fig.5.1.

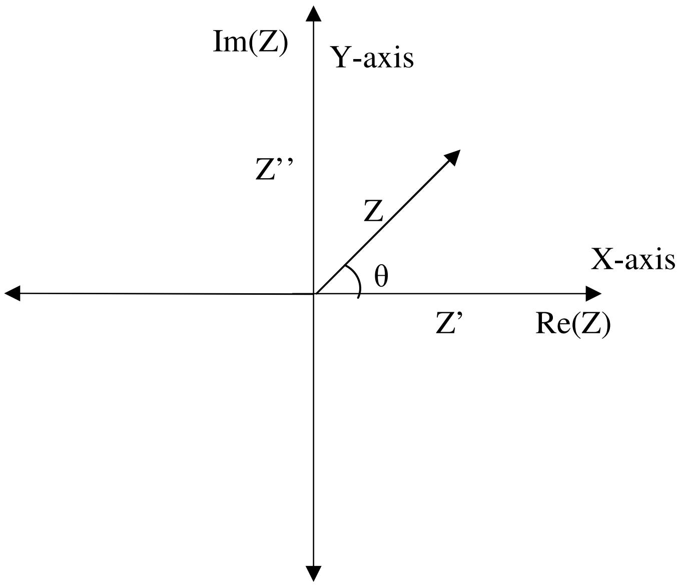


Fig.5.1. *The impedance Z plotted as a planer vector using rectangular and polar coordinates.*

$$Z=Z'+jZ''$$

where, Re(Z)=Z'= $|Z|\cos\theta$, Im(Z)=Z''= $|Z|\sin\theta$ and $\theta=\tan^{-1}\left(\frac{Z''}{Z'}\right)$, the modulus

$$|Z|=[(Z')^2+(Z'')^2]^{\frac{1}{2}}$$

There are several others measured or derived quantities related to impedance, which often play important role in (IS). All of them may be generically called imittances [28]. These are: First is addimitance, $Y=Z^{-1}=Y'+jY''$. In complex domain where v, i, and Z are all taken complex, we can write v=iZ or alternatively i=Yv. It is also customary in IS to express Z and Y in terms of resistance and capacitance components as $Z=R_s(\omega)-jX_s(\omega)$ and $Y=G_p(\omega)+jB_p(\omega)$ where the reactance X_s is given by $X_s=[\omega C_s(\omega)]^{-1}$ and susceptance $B_p=\omega C_P(\omega)$. The other two quantities are usually defined as the modulus function $M=j\omega C_c Z=M'+M''$ and complex dielectric constant or dielectric permitivity $\varepsilon = M^{-1} = \dfrac{Y}{j\omega C_c} = \varepsilon' - j\varepsilon''$, in these expressions $C_c = \varepsilon_0 A_c / l$.

We shall take the general term impedance spectroscopy to include all these other very closely related approaches. Thus, IS also stands for imittance spectroscopy. Impedance spectroscopy is particularly characterized by the measurement and analysis of some or all of the four impedance-related functions Z, Y, M and ε and the plotting of these functions in the complex plane. Such plotting can be very helpful in interpreting small signal ac response of the electrode material being investigated.

A flow diagram of general characterization using impedance spectroscopy (IS) is as depicted in Fig.5.2. Experimentally obtained impedance data for a given electrode material system may be analyzed by using an exact mathematical model based on a plausible, physical theory that predicts theoretical impedance, $Z_t(\omega)$, or by a relatively empirical equivalent circuit whose impedance prediction may be denoted by $Z_{ec}(\omega)$. In either case of the relatively empirical equivalent circuit or of the exact mathematical model, the parameters can be estimated and the experimental data compared to either the predicted equivalent circuit impedance Z_{ec} (ω) or to the exact mathematical model.

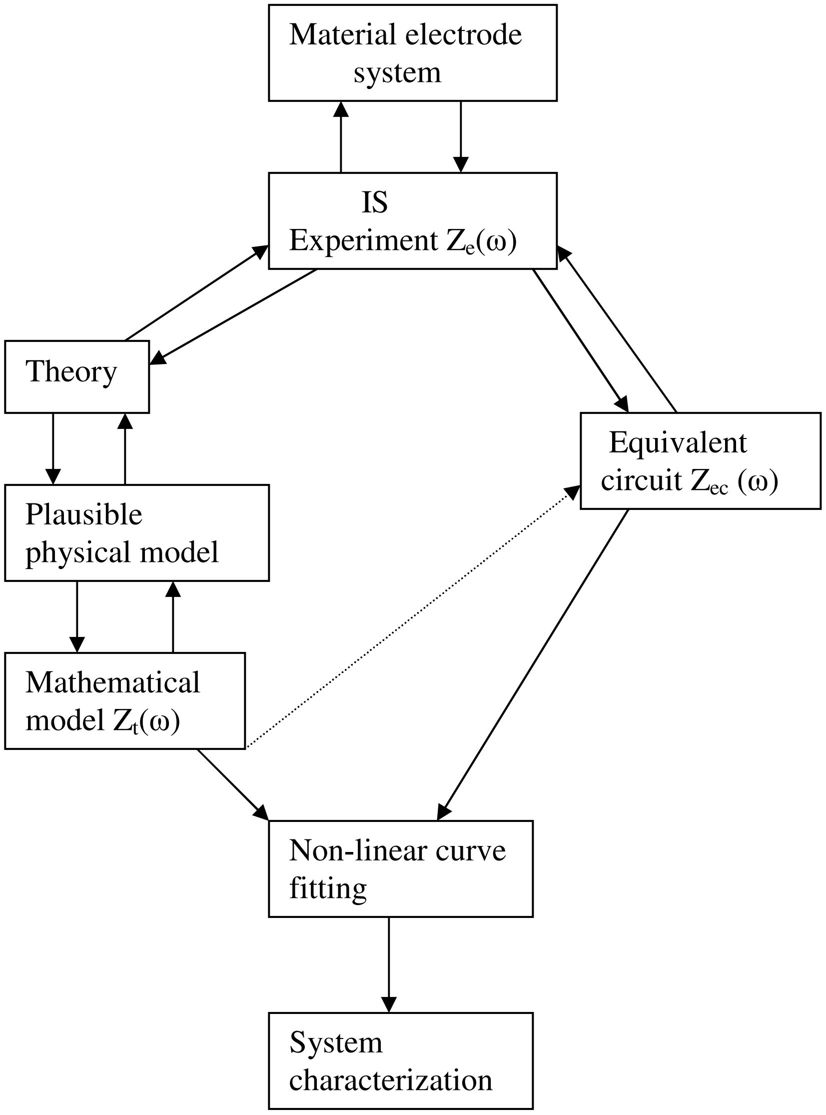


Fig2. *Flow diagram for the measurement and characterization of material electrode [28]*.

4.2. Physical models for equivalent circuit element

A detailed physicoelectrical model of all the process, which might occur in investigations on an electrode-material system, may be unavailable premature, or perhaps too complicated to warrant its initial use. One then tries to show that the experimental data $Z_e(\omega)$ of an equivalent circuit made up of ideal resistors, capacitors, perhaps inductances and possibly various distributed circuit elements. In such a circuit a resistance represent a conductive path, and a given resistor in the circuit might account for the bulk conductivity of the material or even the chemical gap step associated with an electrode reaction. It should be pointed out that ordinary circuit elements such as resistors and capacitors are always considered as lumped-constant quantities, which involve ideal properties. But all real resistors are of finite size and are thus distributed in space; they therefore always involve some inductance, capacitance and time delay response as well as resistance. These residual properties are important over wide frequency range and therefore, usually allow a physical resistor to be well approximated in an equivalent circuit by an ideal resistance, one, which exhibits only resistance over all frequency and yields an immediate rather than a delayed response to an electrical stimulus.

The physical interpretation of the distributed element in an equivalent circuit is somewhat more illusive. They are, however, essential in understanding and interpreting most impedance spectra. In this research the junction between aluminium and polymer is modeled as a simple RC circuit as depicted in the Fig.5.3.

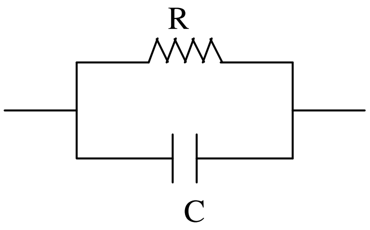


Fig.5. 3. *RC parallel circuit.*

The total impedance of this circuit can be calculated from the knowledge of capacitive reactance (response). The capacitive reactance is given by

$$X_C = \frac{1}{j\omega C}$$

Where ω is the frequency and C is the capacitance of the capacitor.

Therefore, the total impedance is given by

$$\frac{1}{Z} = \frac{1}{R} + \frac{1}{X_C} = \frac{1}{R} + j\omega C$$

After rearranging terms total impedance of the system is given by equation

$$Z = \frac{R}{1 + jR\omega C} = \frac{R}{1 + R^2\omega^2C^2} - \frac{jR^2\omega C}{1 + R^2\omega^2C^2}$$

The Cole-Cole plot of this impedance -Im(Z) vs. Re(Z) in its ideal form is depicted as in Fig.5.4.

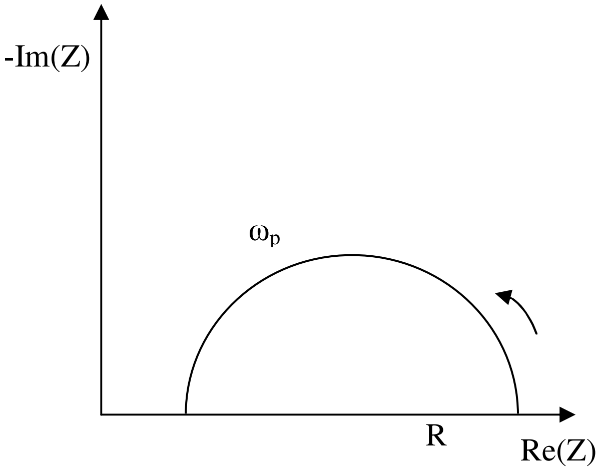
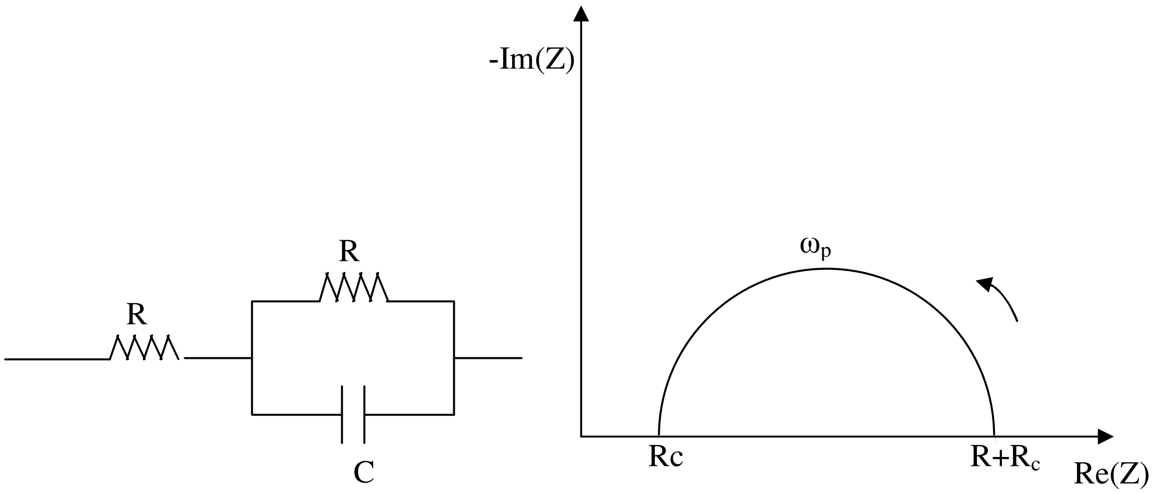


Fig.5.4. *Ideal Cole-Cole plot of parallel RC circuit***.**

The elements of the circuit R and C lead to the time constant $\tau_D = RC$, the dielectric relaxation time of the basic materials. The peak frequency of the complete semi circle of the above figure, ω_p, satisfies $\tau_D\omega_p = 1$. If there is contact resistor, Rc, in series with the RC circuit, the Cole-Cole will be as in Fig.5.5.



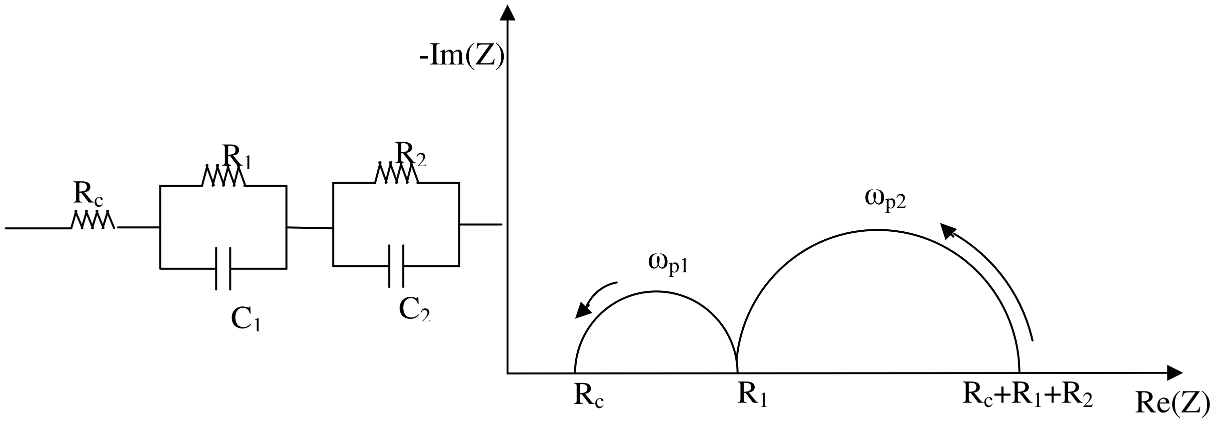
(a) (b)

Fig.5.5. *(a) Parallel RC circuit connected in series with contact resistor (b) its Cole-Cole plot.*

A metal-insulator-semiconductor (MIS) device can also be modeled using an equivalent circuit is the two RC circuits are connected in series to each other see Fig.5.6(a) in addition to the contact resistor. The total complex impedance is given by

$$Z = R_c + \frac{R_1}{1 + jR_1\omega C_1} + \frac{R_2}{1 + jR_2C_2}$$

Where R_1 and C_1 is the resistance and capacitance that is due to the thin insulating film between metal and semiconductors, R_2 and C_2 are that of the depletion region in the semiconductor. The Cole-Cole plot for such a model would be two semi circles whose centers lie on the real axis as shown Fig.5.6.



(a) (b)

Fig.5. 6. *(a) an equivalent circuit model for MIS devices (b) its idealized Cole-Cole plot.*

6. Experiment

Poly[3-(2'-octyloxy-5'-(1'''-oxooctyl)phenyl)thiophene] was supplied by chemistry department of A.A.U. The polymer is dissolved in distilled chloroform to form a solution of concentration 5mg/ml, which was used for absorption spectra and device fabrication for current-voltage and impedance spectroscopy measurement.

For optical absorption measurement thin film of Poly[3-(2'-octyloxy-5'-(1'''-oxooctyl)phenyl)thiophene] was spin coated on clean glass substrates. The thin film of the polymer on glass was then placed in the sample holder of Perkin Elmer λ19 UV/Vis/NIR spectrophotometer. Spectrophotometer is interfaced with computer making use of software called UVCSS, ultra-violet computer spectroscopy.

For electrical characterization, the device is prepared as follows: The ITO coated glass was available in polymer physics laboratory of A.A.U. After the glass is cut out to the appropriate size, the sample glass is partly covered with photoresist. The ITO on the uncovered part of the glass was etched with a mixture of concentrated HCl, HNO_3 and water, 48:4:48 by volume for about 30 minutes. Then the glass was washed successively with acetone, distilled water and rinsed with ethyl alcohol. The final clean glass plate with ITO partly removed is as shown in Fig.6.1.

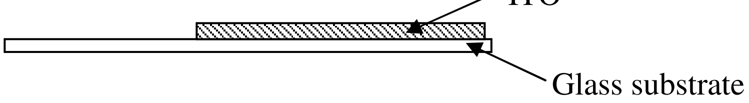


Fig.6.1. *Glass who's ITO is partly removed ready for spin coating*.

The polymer solution is heated above room temperature for small interval of time to remove possible entanglement that the polymer molecules may form. The solution of the polymer is spin coated on the ITO/glass substrate at 6000rpm yielding thin film of polymer spread over the whole glass plate. For electrical contacts a part of the polymer film is removed from the etched part and the ITO part using chloroform, see Fig.6.2.

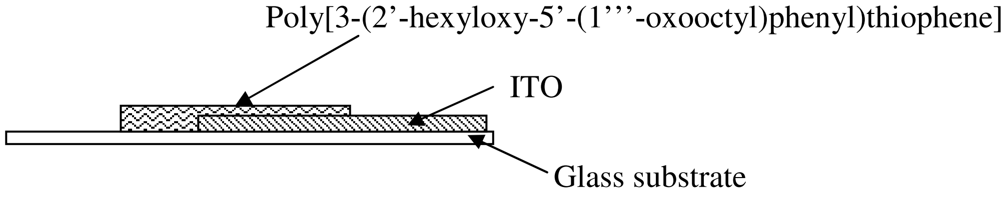
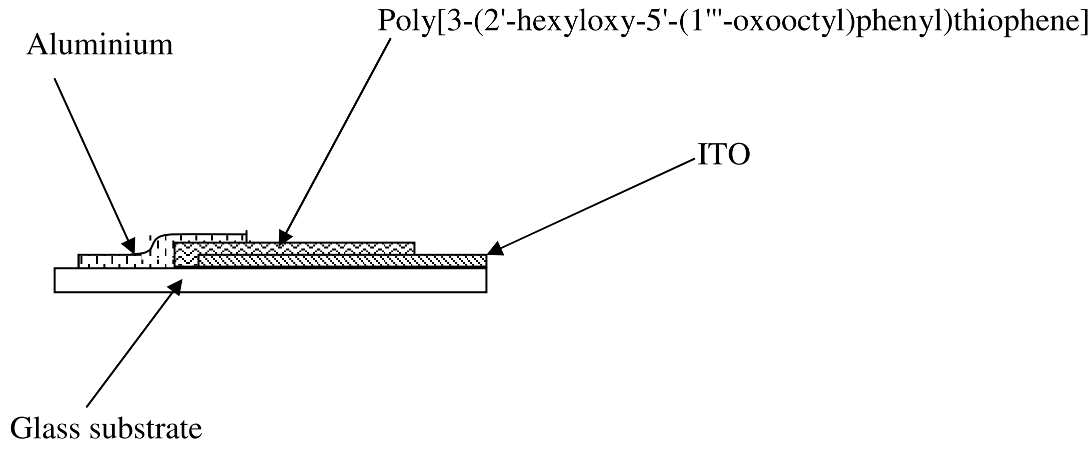
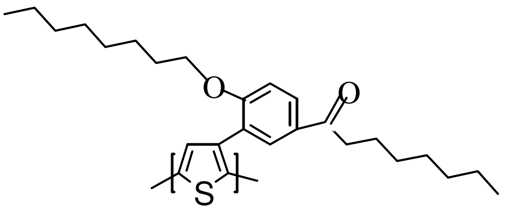


Fig.6.2. *Prepared polymer coated glass ITO structure ready for aluminium deposition.*

Then, the low work function aluminium is deposited on the partly on the polymer film and partly on the clean glass. The deposition was done using Edward Auto 306 vacuum evaporator, at pressure in the chamber of the evaporator is reduced 10^{-6}. The purpose of reducing pressure in Auto vacuum evaporator is to prevent possible oxidation of aluminium that could be formed between aluminium and the polymer. After aluminum is evaporated, the sample was taken out of the chamber for electrical characterization. The final sandwich structure of Al/polymer/ITO sample is depicted in Fig.6.3.





poly[3-(2'-octyloxy-5'-(1'''-oxooctyl)phenyl)thiophene]

Fig.6.3. *Final sample prepared for characterization*

The electrical characterization is done through current- voltage characterization and impedance spectroscopy study.

Current voltage characteristic in the dark was measured by using Hewlett Packard 4140B picoameter. The range of the applied bias was taken from -3V to 3 V in steps of 0.2V.

To study the resistor and the capacitor property of junction between aluminium and the polymer the impedance spectroscopy is found to be very much basic. The measurement of -Im(Z) vs. Re(Z) is made by using the 4192A LF impedance analyzer. The bias voltage was applied from -3V to 3V in steps of 1V. For every bias voltage used, a sinusoidally oscillating voltage of V_{rms} =10mV was applied. The frequency was scanned from 0.5KHz to 2MHz.

7. Result

7.1 Absorption spectrum

The optical absorption spectrum of poly[3-(2'-octyloxy-5'-(1'''-oxooctyl)phenyl)thiophene] is as depicted in Fig.7.1. The polymer absorbs light of wavelength in the range of visible light. The wavelength is scanned from 350nm to 700nm. From the curve the threshold wavelength of absorption is 632nm corresponding to the optical band gap of the polymer is 2.03V. This energy is the minimum energy that is required to excite an electron from the top of the valance band to the bottom of the conduction band of the polymer.

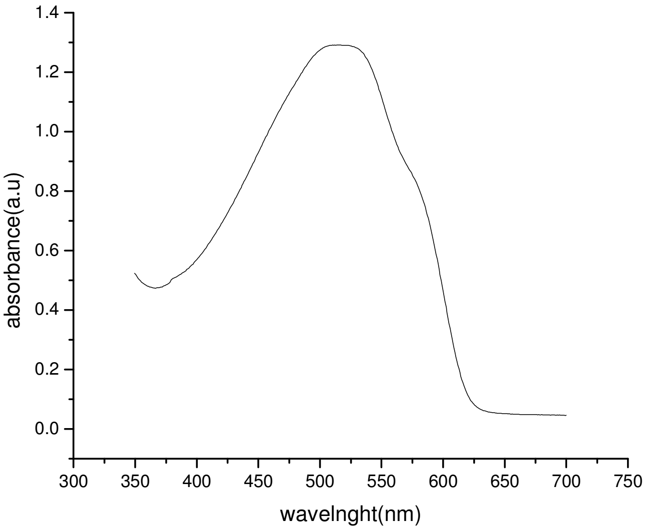


Fig.7.1. *Absorption spectrum of poly[3-(2'-octyloxy-5'-(1'''-oxooctyl)phenyl)thiophene].*

7.2 Current-Voltage Characteristics

Figure7.1.shows the current voltage characteristics at room temperature in the dark of Al/ poly[3-(2'-octyloxy-5'-(1'''-oxooctyl)phenyl)thiophene/ITO sandwich device. The

characteristics indicates non-ohmic, non-rectifying, and nearly symmetrical behavior, see Fig.7.2. The device doesn't allow the current for small biases and allows the current at almost equal rate in both directions. The ratio of current at 3V to -3V is 1.25 showing the symmetry of the curve.

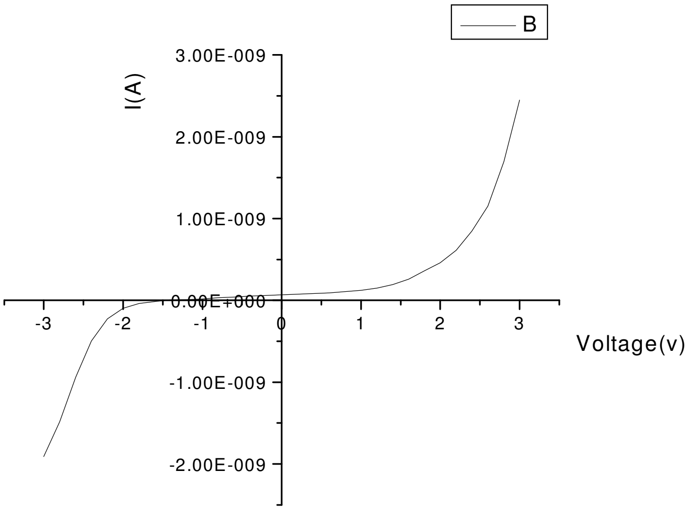


Fig.7.2. *Current versus voltage curves of junction between aluminium and poly[3-(2'-octyloxy-5'-(1'''-oxooctyl)phenyl)thiophene.*

7.3 Complex Impedance Analysis

The sandwich structure of Al/ poly[3-(2'-octyloxy-5'-(1'''-oxooctyl)phenyl)thiophene/ITO device was characterized by measuring complex impedance as a function of frequency and applied bias voltage. The Cole-Cole plots for the sandwich structure are shown in Fig. 7.3. As it can be observed from the graphs, semicircles appeared in the complex impedance plane. The diameters of these semicircles correspond to ohmic resistance.

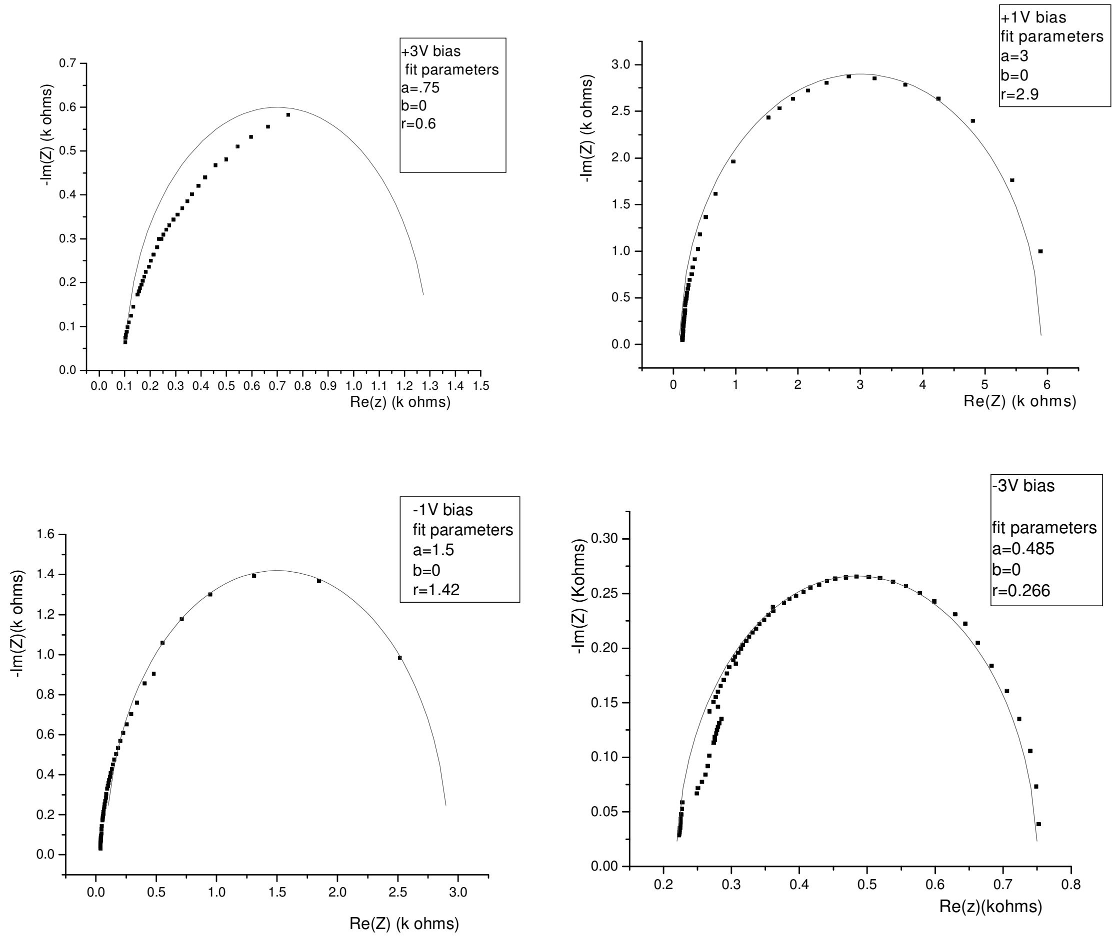


Fig.7.3. *Cole-Cole plots of different biasing voltages with their respective curve fits.*

They yield smaller diameters at +3V and at -3V while the diameter increased at the intermediate voltages. This is reasonably consistent with the symmetric and non-ohmic nature of the I-V curve. The Cole-Cole plots are fitted to semicircles using equation of circle with fit parameters shown on each graphs. The square points are measured coordinates representing the real and the imaginary parts of the complex impedance, and the solid curves are their respective circular fit.

Table 1 Electrical parameters extracted from the Cole-Cole plots of the Al/ poly[3-(2'-octyloxy-5'-(1'''-oxooctyl)phenyl)thiophene] /ITO device.

Bias voltage (V)	R_c(KΩ)	R(KΩ)	C (nF/cm^2)
3	0.1	1.2	20
1	0.14	4.8	30
-1	0.04	2.82	40
-3	0.22	0.532	20

7.4 Discussion

The nature of the polymer under investigation is polythiophene derivative having side chain length of 8 carbon atoms. Comparing the I-V characteristics of other polythiophene derivatives, which have shorter side chain length, the electrical property of this polymer is primarily affected by the length of side chain. Poly[3-(2'-butyloxy-5'-(1'''-oxooctyl)phenyl)thiophene] has side chain length of four carbon atoms and poly[3-(2'-pentyloxy-5'-(1'''-oxooctyl)phenyl)thiophene] has five carbon atoms. These polymers are different from poly[3-(2'-octyloxy-5'-(1'''-oxooctyl)phenyl)thiophene] only in the number of carbon atoms in the side chain. The two polymers with relatively shorter side chains showed rectifying behavior with rectification ratio of 1760 [29] and 48 [30] respectively. These results lead to a conclusion that as side chain length increases, the rectification ratio decreases which is similar to the report on the increase in side chain length of poly(3-alkylthiophene), which showed a decrease in rectification ratio, depletion width and photovoltaic effects [31]. Side chain length affects the electrical properties of polymers in a couple of ways. The decrease in conductivity with increase in side chain length can be attributed to the increased distance for interchain hopping. The decrease in rectification ratio with increase in side chain length indicates a decrease in width of depletion region, which could result in an increase in tunneling current. This means tunneling would be a more likely transport mechanism than emission over the barrier and other transport mechanisms. Therefore, the standard thermionic emission equation, which assumes emission over the barrier as the only transport mechanism, doesn't govern the I-V characteristics of the device.

Studies by photoelectron spectroscopy under ultra-high vacuum have shown that polythiophene derivatives are strongly affected up on Al deposition [5]. During interface formation such reactions lead to the change from sp^2 to sp^3 carbon sites and reorientation of the molecular backbone, which contribute to the loss of conductivity.

8. Conclusion

In this research, optical and electrical properties of poly[3-(2'-octyloxy-5'-(1'"-oxooctyl)phenyl)thiophene] have been investigated. The electrical property was studied by sandwiching the polymer between low work function metal, aluminium, and ITO.

Optical spectroscopy study of poly[3-(2'-octyloxy-5'-(1'"-oxooctyl)phenyl) has shown that the band gap of this organic material is 2.03eV, which is in the range of conventional inorganic semiconductor. This indicates that the polymer is truly semiconducting material.

However, the current-voltage characterization in the dark of the junction between aluminum and the polymer has shown non-rectifying, non-ohmic and nearly symmetrical curve. The ratio of the current at +3V and -3V biases is 1.25, which is almost unity, indicating the symmetry of the curve. Impedance spectroscopy study also revealed the electric property of the polymer to be consistent with the I-V characteristics. The resistance is low for -3V and +3V, and increases for small intermediate bias voltages. Therefore, the junction between aluminium and the polymer forms no Schottky barrier.

Poly[3-(2'-octyloxy-5'-(1'"-oxooctyl) phenyl)] manifested unique electrical properties relative to other polymer, which are polythiophene derivatives and different from it only in the number of carbon atom in the side chain. This property arises predominantly from the length of side chain of the polymer as discussed in the previous section.

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