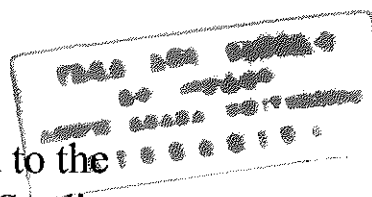


ELECTRICAL PROPERTIES OF JUNCTIONS BETWEEN ALUMINIUM AND POLY(3-OCTYLPHENYLTHIOPHENE) (POPT)

A Thesis presented to the
School of Graduate Studies
Addis Ababa University

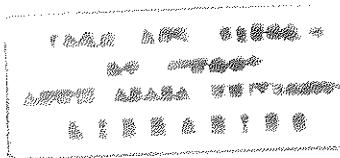


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of Master of Science in Physics

By
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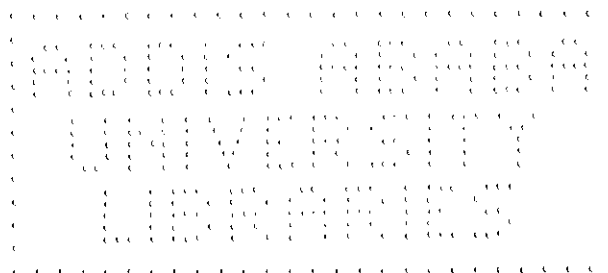


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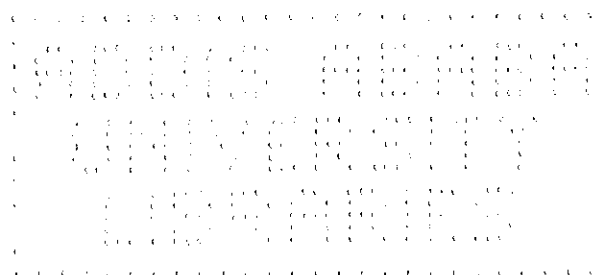
Last, but not the least, I thank the Ministry of education for the sponsorship they granted me to join the School of Graduate Studies.



Abstract

This thesis is based on the study of the electronic properties of poly(3-octylphenylthiophene) (POPT) in the form of Al/POPT/ITO sandwich structure prepared in our laboratory using a vacuum evaporation technique. The electronic properties of the sandwich structure were analyzed using current- voltage characteristics and complex impedance spectroscopy.

The optical absorption spectrum of spin coated thin films of POPT was measured using Perkin Elmer λ 19 UV/Vis/NIR spectrophotometer which showed a forbidden energy gap of about 1.77eV and hence it belongs to the class of semiconducting organic materials. The I-V characteristics of the sandwich structure show a rectifying behavior. The complex impedance analysis exhibits a bias voltage dependent part of a single semicircle in the Cole-Cole plot. This is modeled by one parallel RC electrical circuit, usually obtained from metal-semiconductor (MS) devices.



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1. Introduction

A polymer is made up of many small molecules which are combined to form a single long molecule. The individual small molecules from which the polymer is formed are known as monomers and the process by which the monomers are linked to form a big polymer molecule is called polymerization [1].

Polymers can have different chemical structures, physical properties, mechanical behavior, thermal characteristics, etc., and can be classified in different ways such as:

- Natural and Synthetic polymers
- Organic and Inorganic polymers
- Thermoplastic and Thermosetting polymers
- Plastics, Elastomers, Fibers, and Liquid resins.

While the exact molecular weight required for a substance to be called a polymer is a subject of continued debate, often polymer scientists put the number at about 25,000 g/mol or more. This is the minimum molecular weight required for good physical and mechanical properties for many important polymers [2].

The classification of polymers under the category of insulators is not acceptable after the discovery that conductivity of polyacetylene (PA) can be varied from insulating through semi-conducting to metallic regimes [3]. The research on the application of these polymers, with wide range conductivity, in the field of electronic technology [4], chemical sensors [5], field effect transistor technology [6], micro-muscles [7], and

multi-color polymer LEDs [8] is very promising, owing to the variety of available compounds showing a wide range of chemical and physical properties. In particular, conducting polymers can change optical and electrical properties with doping. This property is important in view of their utilization in the above mentioned areas [4,9]

In this research work we aimed at the investigation of the electrical properties of junction between Aluminium and poly(3-octylphenylthiophene) (POPT). The device on which the work has been done has a sandwich structure of the form Al/POPT/ITO, which is prepared locally. The characterization is done by measuring mainly the current-voltage (I-V) and complex impedance of the diode.

2. Physics and Chemistry of conjugated polymers

2.1 Hybridization

When two hydrogen atoms are brought close enough, the 1s atomic orbitals of the atoms overlap. There are two possible ways in which the wave functions of the electrons in both hydrogen atoms superpose. One of these molecular orbitals (MOs) is of significantly lower energy than the sum of the energy of the original atomic orbitals. It is known as a bonding MO. The other orbital, called anti-bonding MO, is of higher energy than the original atomic orbitals. Energetically the former gives a stable hydrogen molecule, while the latter needs an expenditure of external energy.

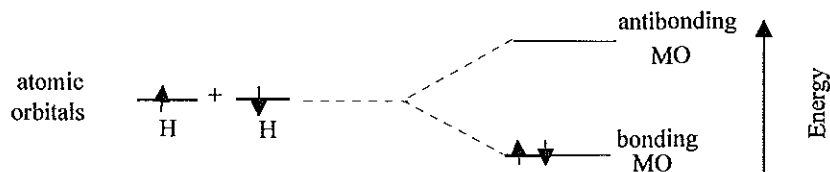


Fig. 2.1 Energy schematics showing the overlap of the 1s atomic orbitals of two H atoms to form bonding and anti-bonding molecular orbitals.

In the electronic structure of organic polymers there is a large energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). This implies an electrically insulating material [10]. Like an atomic orbital, a molecular orbital can be occupied by no more than two electrons. When a covalent bond is formed, the two electrons originally in the atomic orbitals of the separate atoms go into the much lower energy bonding MO. The formation of a covalent bond involves the sharing of only two electrons, i.e., the pair that can be accommodated in the

bonding molecular orbital. Two different geometries are possible [9]. The bonding MOs that result in a geometry cylindrically symmetrical about a line joining the two nuclei involved are called sigma (σ) orbitals, and the bonds formed are called σ -bonds (cf.fig.2.2,A). 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 Fig.2.2,B. This bonding MO is not cylindrically symmetrical about a line joining the two nuclei. It is called a pi (π) bonding molecular orbital. The resultant covalent bond is called a π -bond.

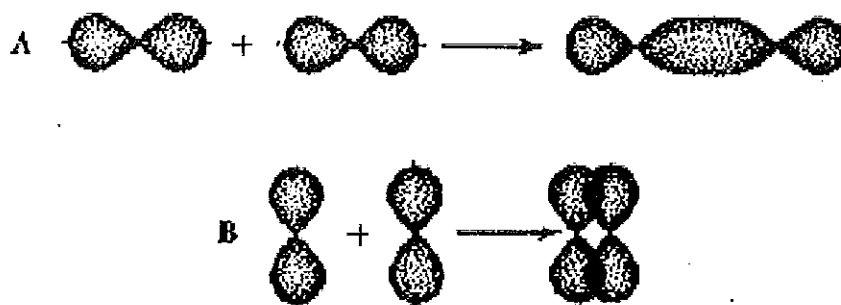


Fig. 2.2 (A) Overlap of two p atomic orbitals to give a bonding σ MO.

(B) Overlap of two p atomic orbitals to give a bonding π MO.

The arrangement of the electrons in the outer most level of carbon when carbon is covalently bonded is not the same as when carbon is in the atomic state. The electronic configuration of carbon in the atomic state is $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$. From this configuration, it would be expected that carbon would form bonds by a combination or overlapping of the two partially filled p orbitals with s and p atomic orbitals of other atoms and thus that the combination with two hydrogen s atomic orbitals would lead to CH_2 . However, the stable hybrid of carbon is methane (CH_4). Furthermore, the four

carbon-hydrogen bonds in CH_4 are equivalent. The equivalent bonding is achieved by hybridization of the one s and three p atomic orbitals in the second energy level to give four orbitals of a new type, which are called sp^3 orbitals. These orbitals are equivalent, and each contains one electron. The four sp^3 hybrid orbitals are directed to the corners of a tetrahedron [11].

The sp^2 hybrid orbitals of carbon occur when it is bonded to three other atoms [11]. The carbon main chain of conjugated polymers consists of covalently bonded carbon atoms. Three of the four valence electron orbitals of the carbon atoms in the conjugated main chain, one s- and two p- atomic orbitals, are hybridized into three sp^2 - orbitals [12,13]. These orbitals form the so called σ -bonds to other carbons, hydrogen, or heteroatoms. The remaining valence electron is in a p_z -orbital oriented perpendicular to the σ -bonds. The p_z -orbitals interact with their neighbors, forming π - bonds between the carbons [10]. We note also that there is an other class of orbital hybridization for triple bond carbons such as acetylene known as sp hybrid orbital [11]

2.2 Peierls Distortion

In organic conjugated polymers, the backbones consist of sp^2 hybridized carbons. This electron configuration results in three σ -bonding electrons, the 2s, $2p_x$, $2p_y$ electrons, and a remaining $2p_z$ electron. The p_z -orbitals interact with their neighbors, forming π -bonds between the carbons. From an organic chemistry point of view, the macromolecule has alternating single and double bonds (σ -bonds and $\sigma+\pi$ -bonds, respectively) along the main chain [10].

The solid state physicist will, however, view this a little differently. Since the inter-chain coupling in these systems is normally weak, the main chain is essentially a one dimensional lattice. Three of the valence electrons form bonds to the neighbors and leave one free electron per unit cell. In the electronic structure that is a half-filled energy band, characteristic of a metal. However, this material is not stable as a metal; a one dimensional system with a half-filled energy band is unstable and will undergo a transition to a dimerized state, leading to a gap at the Fermi energy [14]. This is a Peierls distortion which is a disorder-to-order transition or a metal-to-insulator transition. The energy gap separates the HOMO, which is the valence band, from the LUMO, which is conduction band. The dimerization (metal-to-insulator transition) means that the unit cell will be twice as large as before and will contain two bonds, one long and one short, Fig.2.4. From the appearance of an energy gap in the energy band, we can now expect a semiconductor. In their pure state conjugated polymers are semiconductors or even insulators, with a band gap, E_g , between 1 and 4 eV [10]. Few of them are found in the lower part of this energy range, and therefore, the intrinsic conductivities are low due to small thermal excitation across the band gap. The polymers are often colored since the band gap corresponds to photon energies in the visible region.

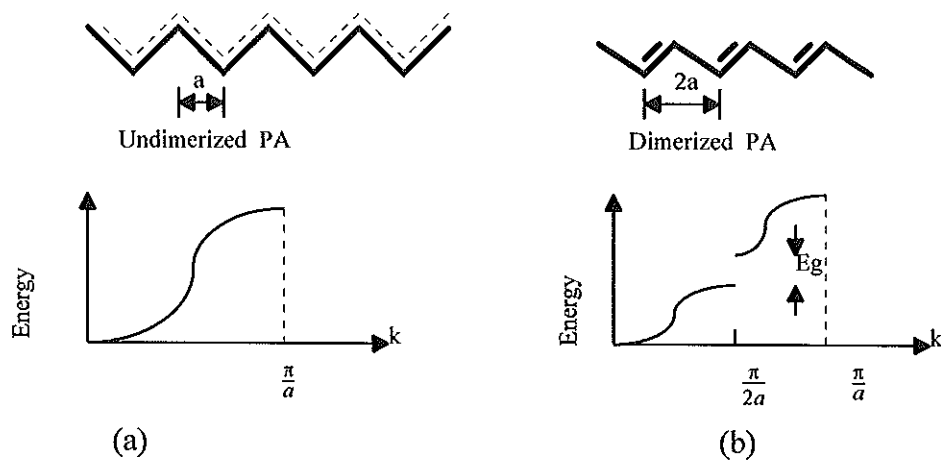


Fig. 2.3 Process of transition from (a) metallic state to (b) non-metallic state by dimerization

2.3 Elementary Excitations

The basic assumption of modern theory of condensed matter is that there exists a stable ground state and excited states of higher energy. In general, the energy of an excited state can be expressed as the sum of energies of elementary excitations or quasi-particles. Just as atoms, ions, and molecules are the building blocks of a crystal in the sense of structure, these elementary excitations are the building blocks of a solid in the sense of motion [15].

2.3.1 Solitons in polyacetylene

The conjugated polymer with the simplest structure is polyacetylene. It has only a main chain of alternating single and double bonds between carbon atoms, with one hydrogen

atom attached to every carbon. Fig. 2.4 shows two degenerate ground states of trans-polyacetylene.



Fig. 2.4 Degenerate ground states of trans-polyacetylene

Putting two such trans-polyacetylene chains together, a phase transition region will occur where the chain has an apparent bond alternation defect, see Fig. 2.5. This defect, called a soliton and often referred to as being a quasi-particle, corresponds to an unpaired electron and gives rise to a localized electronic state in the middle of the otherwise forbidden energy gap [16].



Fig. 2.5 Creation of a soliton in trans-polyacetylene.

Apart from the neutral soliton, addition or withdrawal of an electron creates the following charge and spin configurations, fig.2.6.

Charge 0	Charge +e	Charge -e
Spin $\frac{1}{2}$	Spin 0	Spin 0
Neutral Soliton	Positive Soliton	Negative Soliton

Fig. 2.6 Charge and spin combinations for differently charged solitons.

2.3.2 Polarons and Bipolarons

The term polaron is known from inorganic semiconductors to describe an elementary excitation resulting from the effect of motion of an electron in an ionic crystal. In simple terms, an electron moving in an ionic crystal attracts the positive ions and repels the negative ones. Hence it polarizes its surroundings. The polarization field thus produced, in turn, affects the motion of the electron itself. This set of the moving electron and its accompanying polarization field is called a polaron [17].

Conjugated polymers can also be built from aromatic units. Pyrrole, thiophene, and benzene are examples of monomers from which non-degenerate ground state conjugated polymers can be synthesized. In these polymers there are two different possible bond alternations, since all carbon atoms are not in equivalent positions. This is synonymous with a non-degenerate ground state. The two different bond alternation patterns are referred to as aromatic and quinoidal. The aromatic form is the lowest energy state. For instance, the left and the right sides of the soliton in polythiophene, as depicted in fig. 2.7, have different energies.

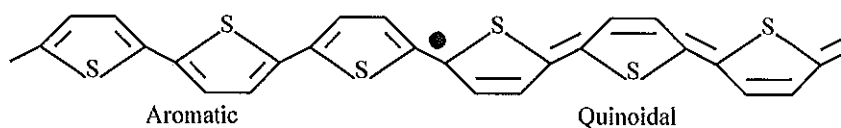


Fig. 2.7 Soliton site in a polythiophene.

Contrary to solitons in polyacetylene, which are more stable and can be positioned anywhere in the chain, solitons in non-degenerate polymers are energetically unstable. They move along the chain, thereby changing the high energy quinoidal rings into low

energy aromatic rings. If defects in non-degenerate ground state polymers are to be stable, bound stable defects must be created. This bound double-defect (quasi-particle) is called polaron if singly charged, fig.2.8(a) and bipolaron if doubly charged, fig.2.8(b) [16].

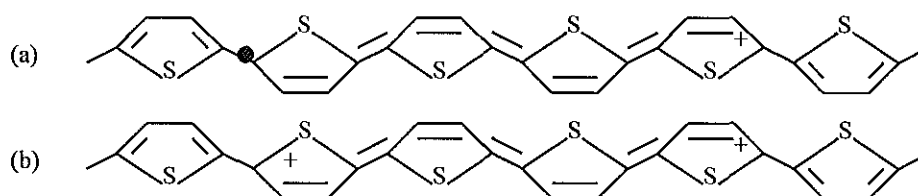


Fig. 2.8 A polaron (a) and bipolaron (b) in polythiophene.

In the same way as solitons, which can be related to the polarons and bipolarons because a polaron can be regarded as a combination of a soliton and an antisoliton, the polaronic defects give rise to states in the band gap, fig. 2.9. These new states resulting from solitons, polarons, and bipolarons can be observed in optical absorption spectra [18-20] because new transitions become possible.

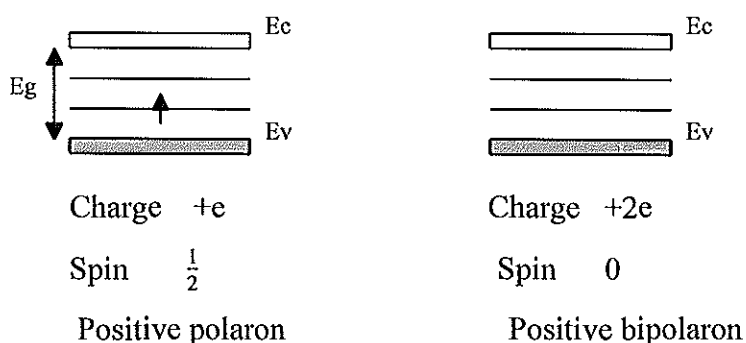


Fig. 2.9 Energy band diagrams showing charged states of a non-degenerate ground state polymers.

3. Conducting polymers

3.1 Review

The band structure of solids is used to classify solids as conductors, semiconductors and insulators. Based on this classification polymers were classified under the category of insulators before 1970's. However, after the discovery of conducting polyacetylene (CH)_x, [21], it has become difficult to categorize (CH)_x, or PA because its conductivity varies from insulating through semi-conducting to metallic [3].

Conjugated polymers have, in their pure undoped state, a very low electronic conductivity. The conductivity is of the order of 10^{-8} S/cm and can be explained by the very small thermal excitation of charge carriers over the band gap [10]. The conductivity can however be raised dramatically by the introduction of charge carriers on the polymers chains. This is done by doping of a polymer with acceptor or donor species. The electrical conductivity of conjugated organic polymers can now be varied over almost the full range of conductivity as depicted in fig.3.1

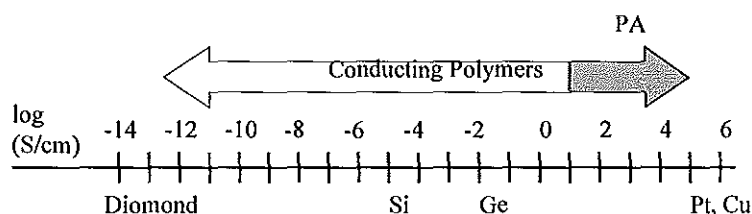


Fig. 3.1 Range of conductivities of polymers compared with conductivities of other materials at room temperature [9].

Such a wide range of conductivity of polymers makes it possible to use polymers for different applications. The work in the field of conductive polymer has become highly interdisciplinary with scientists coming from different areas such as physics, chemistry, materials science, biochemistry, and electrical engineering, all trying to understand the intrinsic behavior and properties of these polymers and how to utilize this knowledge in new applications. The following are some of the conducting polymers on which the work for further study and application is continued [16].

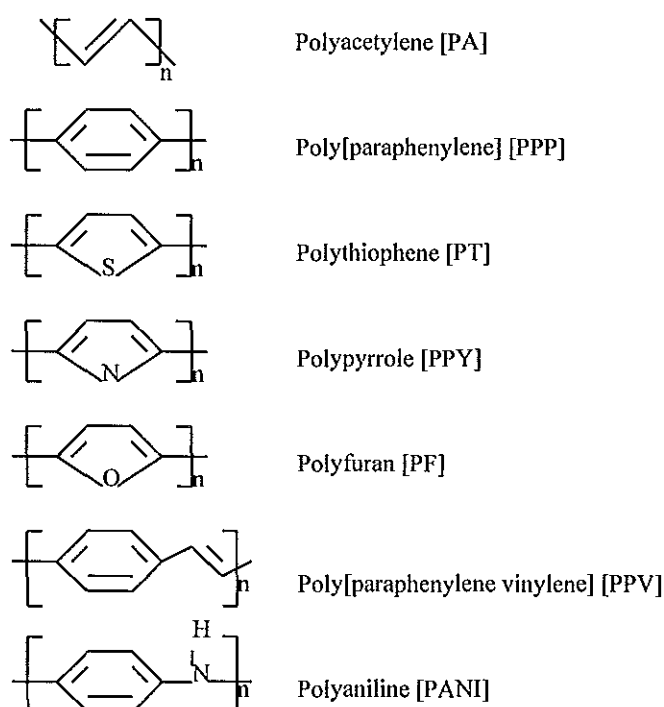


Fig. 3.2 Examples of conjugated polymers

One of the major problems when developing and improving these materials is that the polymers have limited processability and stability [16]. Extensive work is being done to improve the conductivity, processability and stability of polymers. To this end, there has been a successful effort in attaching alkyl chains to polymers like polythiophenes to make

it soluble in organic solvents. Attaching side chains or rings does not change the electrical properties of conjugated polymers [22].

Some of the substituted polythiophenes are depicted in fig. 3.3

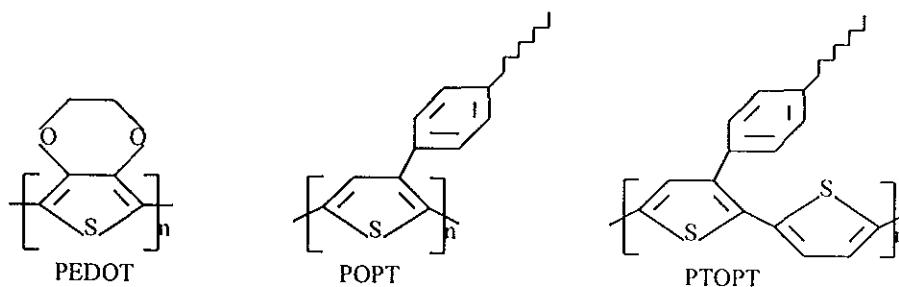


Fig. 3.3 Chemical structures of some substituted polythiophenes.

POPT is the candidate for this research work while the electronic properties of PEDOT and PTOPT are studied by Dr. Bantikassegn [23,24]. The electronic and optical properties of PTOPT are shown in the following figures [24]:

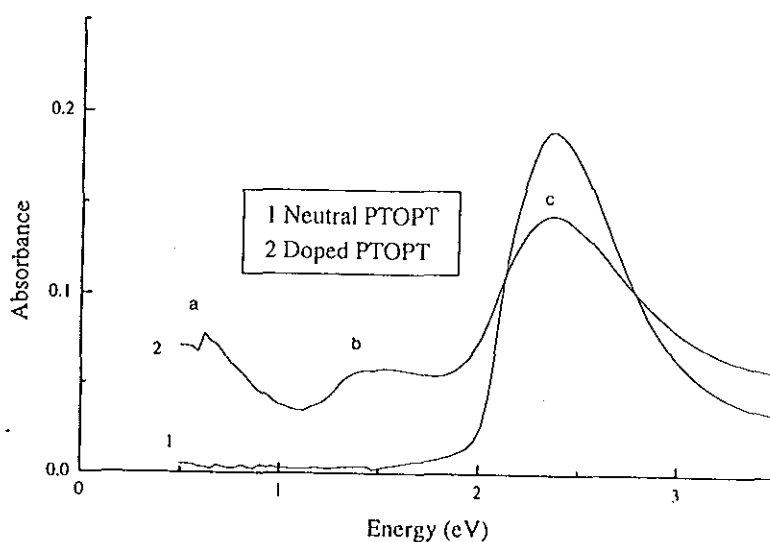


Fig. 3.4 Optical absorption spectra of PTOPT [24].

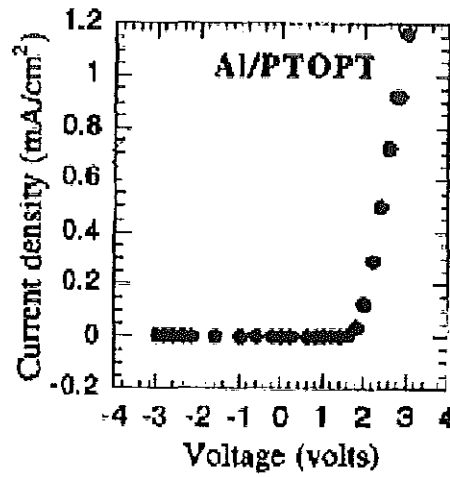


Fig. 3.5 J-V Characteristics of PTOPT [24].

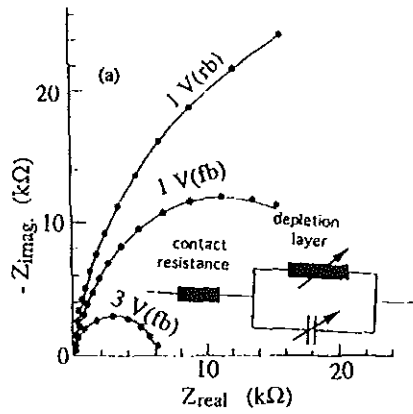


Fig. 3.6 Cole-Cole plots of Al/PTOPT/ITO diodes for PTOPT [24].

From the above figures, it is concluded [24] that

- neutral PTOPT has an energy gap of about 2 eV.
- the J-V measurements on ITO/PTOPT/Al structures show a Schottky barrier diode.
- the complex impedance measurement clearly shows that a single RC element equivalent circuit is sufficient to account for the diode. There is no extra layer at the interface.

3.2 Charge transport mechanism

The classification of materials may be effected using various criteria. One of them is the behavior of materials under the application of an external voltage [25]. According to this criterion materials in various states of aggregation (gases, liquids, solids) may be classified as insulators, semiconductors, or conductors (metals) and nowadays superconductors as well. As a further classification criteria a dependence of the electrical conductivity on the changes in temperature may be used. If a pure metal is cooled, the conductivity will increase, because the lattice vibrations which act as obstacles for the charge carriers freeze out. If a crystalline semiconductor is cooled, the conductivity will decrease. In this case not only the lattice vibrations (approximately linear with temperature) freeze out, but also the charge carriers. The latter effect dominates because it is exponential due to the presence of an energy gap in the electronic excitation spectrum. Between pure metals and crystalline semiconductors there are dirty metals and amorphous semiconductors. In a dirty metal the relevant obstacles for carrier motion are lattice defects and impurities. Their concentration does not depend on the sample temperature and therefore the conductivity is nearly constant. In an amorphous semiconductor and in some very disordered metals there is no continuous carrier motion at all. The carriers are localized and can only move with the help of lattice vibrations. Consequently here the conductivity increases with increasing temperature, but it does not increase as fast as in a crystalline semiconductor, because there is no gap across which the carriers have to be excited [25].

Conducting polymers behave more like amorphous semiconductors, where the electrons

are not moving in bands but are located at specific states in the gap. They hop between these localized states. "Hopping" is an abbreviation for "phonon assisted tunneling" [26]. The charge transport process of a conjugated polymer cannot be described by one single model over the whole conductivity range, from insulating to metallic. Different models need to be applied to different polymers in various conductivity regions. The different conductivity regions are due to different levels of doping. For undoped or lightly doped conjugated polymers, the electronic properties show a behavior, with zero conductivity at 0K. The charge transport is then explained by hopping between localized solitonic, polaronic or bipolaronic states according to Mott's variable range hopping (VRH) theory [27]. The VRH theory assumes that the localization of the states is weak, allowing electrons to jump further away than to the nearest available site, thereby making it possible for them to find a state with lower energy than the nearest neighbor state. The term variable range describes this flexibility in finding an appropriate site. When the temperature increases, the number of available states rises and the average hopping distance decreases, resulting in a higher conductivity. The temperature dependence of the electrical conductivity is described by

$$\sigma = \sigma_0(T) \exp\left[-\left(\frac{T_0}{T}\right)\right]^\alpha \quad (3.1)$$

$$\text{where } \alpha = 1/(1+d) \quad (3.2)$$

d is the dimensionality of the system, $d = 1, 2, 3$

$\alpha_0(T)$ varies more slowly than the exponential factor, and the characteristic

temperature T_0 is related to the density of states $N(E_F)$ and the localization length

' a ' as

$$T_o \propto \frac{1}{a^d N(E_F)} \quad (3.3)$$

When going to higher doping levels, a model with small conducting islands with metallic conductivity separated by insulating barriers is used. These barriers could be different kinds of inhomogeneities like conjugational defects or undoped chain segments. Charge transport through the material will then be limited by the fact that charge carriers have to tunnel through these barriers. The most successful theories so far describing this type of conductivity have been presented by Sheng [28-31]. The model gives the temperature dependence of the conductivity

$$\sigma(T) = \sigma_o \exp\left[-\frac{T_1}{T_o + T}\right] \quad (3.4)$$

where the constants T_o and T_1 are determined by the shape and size of the insulating barriers. A metallic conductivity is found at low temperatures in highly doped conjugated polymers. By metallic, one usually means the existence of a finite or increasing conductivity as T approaches 0K, which has recently been observed in polypyrrole [32] and polyaniline [33], where an insulator to metal transition occurs.

For the intermediately doped conjugated polymers the situation is more complicated with probably a number of different conduction mechanisms taking place simultaneously [16].

4. Electrical properties of Metal-Semiconductor contacts

Metal contacts to semiconductors form interfaces that manifest basic features of many rectifiers, metal-semiconductor devices such as field-effect transistors, sensors, and other surface junction devices [34]. Hence electrical contacts to semiconductors are critical elements in a number of important technologies.

When a metal is making intimate contact with a semiconductor, the Fermi levels in the two materials must be coincident at thermal equilibrium [35,36]. Depending on the work functions of the metal and semiconductor, the MS contacts may be either ohmic or non-ohmic. In the latter case, the interface may be a rectifying (Schottky) contact [9].

4.1 Current-Voltage Characteristics

The current transport in a metal-semiconductor junction is due mainly to majority carriers. The transport equation of an ideal metal semiconductor rectifying contact is given by a Schottky barrier diode equation [35].

$$J = J_o \left[\exp\left(\frac{qV}{nkT}\right) - 1 \right] \quad (4.1)$$

where J is the total current density, J_o is the value of the reverse saturation current density, q is the charge of an electron, V is the applied voltage, k is Boltzmann's constant, T is absolute temperature and, n is diode quality factor.

Case 1. If $J_0 \ll J$, the contact will effectively block current flow for one sign of applied voltage (known as the reverse bias) and will display an exponentially increasing current when the bias voltage is of the opposite polarity (called the forward bias).

Case 2. If $J_0 \gg J$, the junction will readily pass current for both signs of the applied voltage. In eqn. (4.1), if $J_0 \gg J$, then the exponential can be expanded to yield:

$$V = \left(\frac{nkT}{qJ_0} \right) J \quad (4.2)$$

This equation is a linear, ohmic response displayed by the metal/semiconductor contact system.

Both ohmic and rectifying contacts are described for many semiconductor applications. For example, ohmic contacts are necessary to avoid resistance losses for almost all types of semiconductor structures [35]. Rectifying contacts are desirable for photovoltaic cells [37], photodetectors [35], field effect transistors [35], chemical sensors [38], and numerous other semiconductor devices.

Case 3. If J_0 is comparable to J (neither of these extreme cases), the J-V characteristics is non ohmic and non rectifying, where the plot of V vs. J will show a symmetrical curve.

When a metal of a given work function is brought into contact with a semiconductor having different work function, charge will flow across the interface in order for the Fermi level to become a constant through out the system in equilibrium [35]. The

magnitude and direction of this initial charge transfer will determine the electrical properties of the device.

As depicted in Fig.(4.1) the metal/semiconductor (p-type) contact will give either an ohmic or rectifying junction depending on the work functions of metal and semiconductor (p-type) [39].

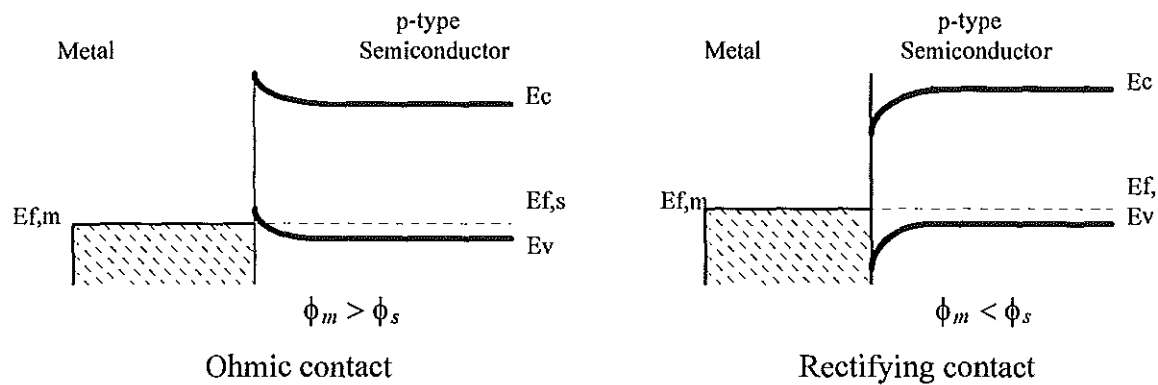


Fig. 4.1 Contacts between metal and p-type semiconductor where ϕ_m is work function of metal and ϕ_s is work function of semiconductor.

The same phenomena are observed [40] for a p-type semiconducting polymer-metal interface. Important parameters in the analysis of metal-semiconductor contacts can be extracted from an idealized n-type semiconductor/metal contact as shown in Fig.(4.2)

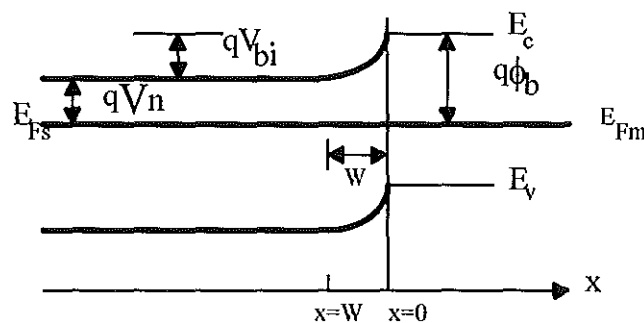


Fig. 4.2 Energy band diagram at equilibrium with important parameters defined

where W is the depletion width, qV_n is the difference between E_c and E_F in the bulk of the semiconductor, V_{bi} is the built-in potential of the junction and ϕ_b is the barrier height, $\phi_b = V_n + V_{bi}$.

For inorganic semiconductor/metal contacts, an explicit relation-ship between the barrier height ϕ_b and J_o can be obtained from thermionic emission/diffusion theory [35] as:

$$J_o = A^{**} T^2 [\exp(\frac{-q\phi_b}{kT})] \quad (4.3)$$

where A^{**} , which is known as the modified Richardson constant, expresses [9] the number of electrons at the semiconductor/metal interface which may be injected into the metal. A^{**} also takes into account the effective density of states in the conduction band, the effective mass of the electron in the semiconductor, phonon scattering, and quantum mechanical reflection at the semiconductor/metal interface. The Richardson constant for an electron in free space is $A = 120 \text{ A/cm}^2\text{K}^2$.

For organic semiconductor Schottky diodes, the modified Richardson constant is assumed to be that of a free electron, namely $A^* = 120 \text{ A/cm}^2\text{K}^2$ [41,42]. Experimentally, J_o is obtained by extrapolating the linear part of the plot of $\ln J$ vs. V and taking the intercept with the J axis. Then the value of ϕ_b is calculated using Eqn. (4.3).

4.2 Capacitance-Voltage Measurements.

Another way of determining the barrier height in the case of a rectifying

metal-semiconductor diode is the measurement of the capacitance of such a contact [35]. The capacitance C of the depletion layer (cf.Fig. 4.2) of a reverse biased semiconductor is given by :

$$C = A_s \left[\left(\frac{q\epsilon_s N_d}{2} \right)^{\frac{1}{2}} \left(\phi_b - V_n - V - \frac{kT}{q} \right)^{\frac{-1}{2}} \right] \quad (4.4)$$

where A_s is the cross-sectional area of the device, ϵ_s is the dielectric constant of the semiconductor, N_d is the dopant density, V is the applied voltage and kT/q is the thermal energy.

If we rearrange the above equation we get:

$$\frac{1}{C^2} = \left[\frac{2}{qA_s^2 \epsilon_s N_d} \left(\phi_b - V_n - V - \frac{kT}{q} \right) \right] \quad (4.5)$$

where c is capacitance per unit area.

A plot of $1/C^2$ as a function of V gives a straight line. Then one can determine:

- the barrier height from the intercept with the voltage axis and
- the dopant concentration from the slope of the graph.

The above discussion is limited to a diode formed from an ideal interface between a metal and a semiconductor with no interfacial layers of any kind separating them. However, the case of metal-insulator-semiconductor diode is of a paramount importance in device physics [35]. Such a structure is reported [23,43] for conjugated polymer-metal junctions.

4.3 Impedance spectroscopy

Impedance Spectroscopy (IS) appears destined to play an important role in fundamental

and applied electrochemistry and materials science. In a number of respects, it is a powerful method of characterizing many of the electrical properties of interfaces of various substances with electronically conducting materials. It is also used in a medium that conducts ionically, electronically, e^-/h^+ or mixed electronic plus ionic conduction [43,44]. There are various types of electrical responses which are used in IS, out of which we focus only on the technique which is standard and most common that enables us to measure impedance directly as a function of frequency and applied voltage.

Suppose that a voltage signal $V(t)=V_m \sin(\omega t)$, with a frequency $\omega = 2\pi f$, is applied to the device under test (DUT) and the resulting response of current $I(t)=I_m \sin(\omega t + \theta)$ is measured, where θ is the phase difference between the voltage and the current. $\theta = 0$ for pure resistors and $\theta = \pi/2$ for pure capacitors. Thus a combination of a resistor and a capacitor in a network will have $0 < \theta < \pi/2$. The conventional impedance is defined as $Z(\omega) = V(t)/I(t)$, with $\theta = \theta(\omega)$. Mathematically it is represented by a rotating vector diagram (phasor) in a complex rectangular or polar coordinate system. In an orthogonal system, its magnitude and direction can be obtained from the relation $Z = Z' + jZ''$, where $j = \sqrt{-1} = \exp(j\pi/2)$

There are several other measured or derived quantities related to impedance which often play important roles in IS. All of them may be generally called immittance. The relation between the four basic immittance functions, namely, the impedance Z , the admittance Y , the modulus M and the dielectric permittivity ϵ for a sample containing only a capacitor with capacitance C is summarized as shown below.

	M	Z	Y	ϵ
M	M	μZ	$\frac{\mu}{Y}$	$\frac{1}{\epsilon}$
Z	$\frac{M}{\mu}$	Z	$\frac{1}{Y}$	$\frac{1}{\mu\epsilon}$
Y	$\frac{\mu}{M}$	$\frac{1}{Z}$	Y	$\mu\epsilon$
ϵ	$\frac{1}{M}$	$\frac{1}{\mu Z}$	$\frac{Y}{\mu}$	ϵ

where $\mu = j\omega C$

Table 4.1 Relations between the four immittance parameters.

In impedance spectroscopy, Z and Y are usually expressed in terms of resistive and capacitive components as $Z = R_s(\omega) - jX_s(\omega)$ and $Y = G_p(\omega) + jB_p(\omega)$, where the reactance $X_s(\omega) = [\omega C_s(\omega)]^{-1}$, the susceptance $B_p = \omega C_p(\omega)$, and the subscripts s and p stand for "series" and "parallel".

Cole-Cole analysis shows that the complex impedance $Z = Z' + jZ''$ (as well as Y, M and ϵ) may be plotted in a complex plane (Argand diagram). Thus the phase angle $\theta = \tan^{-1}(Z''/Z')$.

Modeling concepts: One of the most attractive features of impedance spectroscopy lies in its applicability to the studies aimed at the development of direct correlation between the response of a real system and an idealized model circuit composed of discrete electrical components [45]. In the modeling studies one seeks to match experimental impedance with an equivalent circuit composed of ideal resistors and capacitors.

Phenomenologically, a resistor (R) is taken to represent the dissipative components of the

dielectric response, while a capacitance (C) describes the storage components of the dielectric material, that is, its ability to store energy in the electric field. Resistances and capacitances can be combined in a variety of forms, leading to an array of phenomenological models that can describe various combinations of polarization mechanisms in dielectric materials. Inductance (L) requires the storage of energy in a magnetic field but there is no appreciable AC magnetic field - energy present in the low current (mA) impedance spectroscopy measurements.

i) Consider an RC parallel circuit shown below

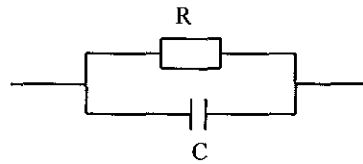


Fig. 4.3 RC parallel circuit

The impedance is then given by

$$Z = \frac{R}{1+j\omega RC} \quad (4.6)$$

but $RC = \tau$, which is the relaxation time. Therefore

$$Z = \frac{R}{1+j\omega\tau} \quad (4.7)$$

Separating equation (4.7) into real and imaginary parts yields

$$Re[Z] = \frac{R}{1+\omega^2\tau^2} \quad (4.8)$$

$$-Im[Z] = \frac{R\omega\tau}{1+\omega^2\tau^2} \quad (4.9)$$

substituting $\omega\tau = \tan(\theta)$ yields:

$$\text{Re}[Z] = R \cos^2(\theta) \quad \text{and} \quad (4.10)$$

$$-\text{Im}[Z] = R \sin(\theta)\cos(\theta) \quad (4.11)$$

Using a trigonometric identity we can write equations 4.10 and 4.11 as

$$\text{Re}[Z] = \frac{R[1+\cos 2\theta]}{2} \quad (4.12)$$

$$-\text{Im}[Z] = \frac{R[\sin 2\theta]}{2} \quad (4.13)$$

The maximum value of $-\text{Im}(Z)$ is attained for $\theta = 45^\circ$ in which case $-\text{Im}[Z] = R/2$ and $\omega\tau=1$. Then the diameter of the semi-circle corresponds to R . The Cole-Cole plot of this circuit will be a semi-circle whose center lies on the $\text{Re}[Z]$ axis [46].

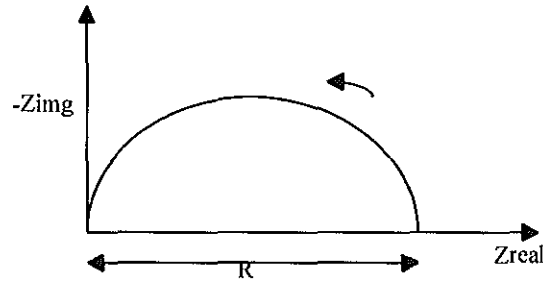


Fig 4.4 Cole-Cole plot of RC parallel circuit

If we add a resistance R_c in series to the above model the impedance will be given by

$$Z = R_c + \frac{R}{1+j\omega RC} \quad (4.14)$$

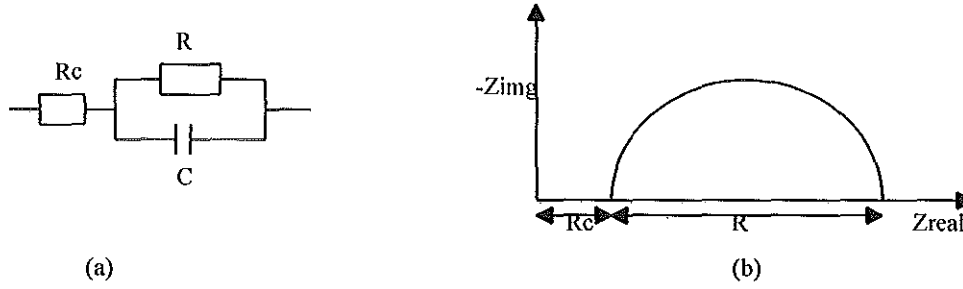


Fig. 4.5 Combination of the resistances R_c , R and capacitance C (a) and Cole-Cole plot of impedance Z of the circuit in the complex plane (b).

Note that the circuit represented by Fig.4.5 (a) is an equivalent circuit model for a junction between a metal and a semiconductor in which the depletion region accounts for the observed capacitance and resistance and R_c accounts for the observed contact resistance at infinite frequency [23,34].

ii) Another important RC circuit is given in Fig.(4.6) below. This is an equivalent circuit which is used to model a metal-insulator-semiconductor (MIS) device [23].

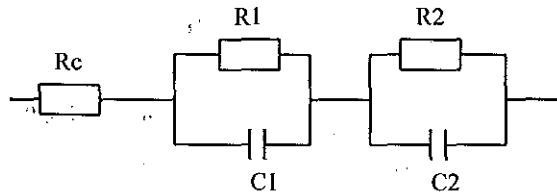


Fig. 4.6 An equivalent RC circuit of MIS device.

The complex impedance of the above circuit is given by:

$$Z = R_c + \frac{R_1}{1+j\omega R_1 C_1} + \frac{R_2}{1+j\omega R_2 C_2} \quad (4.15)$$

where R_c is the series contact resistance, R_1 and C_1 account for the resistance and capacitance of an interfacial insulating thin layer and R_2 and C_2 are for the depletion

region.

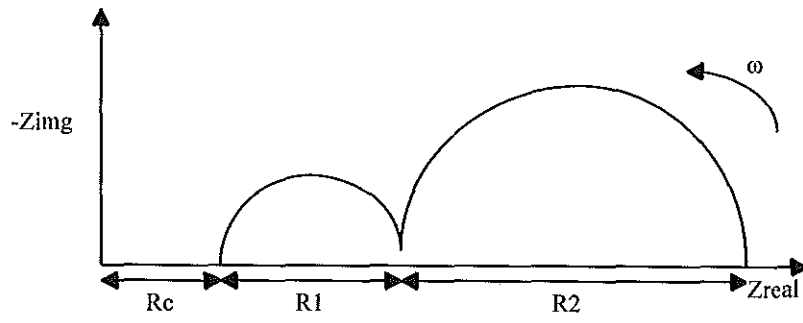


Fig. 4.7 Idealized Cole-Cole plot for a circuit shown in Fig. 4.6

5. Instrumentation and Experiment

5.1 Instruments: In this section we will briefly discuss about the instruments that we have used for our research.

5.1.1 Sartorius: This is a standard high-precision and high-quality weighing instrument [47]. The balance is designed to provide reliable weighing results in the laboratory and in industry with an accuracy of 0.1 mg. We used this instrument to weigh the polymer, POPT, in order to determine its concentration in chloroform solution.

5.1.2 The spinner system: This is a photoresist coater model 4000. It consists of a bench top spinner unit and a remote control unit which can be located outside the immediate work area. It spins the wafers on a DC motor driven chuck at speeds that can be selected between 100 and 6200 rpm [48]. It is used to spin coat the polymer solution on the ITO/glass substrate. The thickness of the deposited polymer is controlled by the rate of the revolution and concentration. For a given concentration of polymer solution, the higher the speed (rpm), the thinner the deposited polymer film.

5.1.3 Edwards Auto 306 Vacuum Depositor: The Auto 306 is a microprocessor controlled vacuum coater that can be arranged in a variety of coating tasks. It is designed for thermal vapor deposition processes under high vacuum, of the order of 10^{-7} Torr [49]. It is used to deposit aluminum on the POPT/ITO/glass substrate at a pressure of approximately 6.5×10^{-6} Torr.

5.1.4 Perkin Elmer λ 19 Spectrophotometer: It is a fast and powerful machine for measuring the reflectance, transmittance and absorbance of layers as a function of wavelength or energy. The PE λ 19 spectrophotometer allows spectral measurements between 170nm and 3200nm [50]. It is a computer interfaced instrument with a software, UVCSS (UV computerized spectroscopy software). We used this instrument to measure the absorption spectrum of POPT.

5.1.5 HP model 4140B pA meter/DC Voltage Source: It comprises a high stable pico-ampere meter with 10^{-15} A (max.) resolution coupled with two programmable DC voltage sources. Its application is not limited in the measurement of small leakage current of semiconducting devices but also for making insulation resistance/leakage and current absorption measurement/analysis of capacitance [51]. It can automatically synchronize measurement timing between the pA section and the voltage source section when the function is set to I-V mode. The DC voltage source has an output range between -100V and +100V. It is generated either in the stair case or ramp mode. The sweep can be done automatically or manually. The start, stop or step voltages can be set from -100V to +100V at 100mV resolution or from -10V to +10V at 10mV resolution.

5.1.6 HP 4192A LF Impedance Analyzer: It is a fully automatic, high performance test instrument designed to measure a wide range of impedance parameters as well as gain, phase, and group delay [52]. It can provide measuring frequency, OSC level, and dc bias voltage (impedance measurements only) equivalent to actual operating conditions. The sweep capability of the built-in frequency synthesizer and dc bias source permits quick and accurate measurements. The built-in frequency synthesizer can be set to measuring

frequency within the range from 5Hz to 13MHz with 1mHz maximum resolution. OSC level is variable from 5mV_{rms} to 1.1V_{rms} with 1mV resolution (5mV for levels higher than 100mV). The internal dc bias voltage source (impedance measurements only) supplies voltage from -35V to +35V in 10mV increments. Measuring frequency or dc bias voltage can be automatically or manually swept in either direction. OSC level can be manually swept in either direction in 1mV increments.

In impedance measurements, the HP 4192A LF impedance analyzer can measure eleven immittance parameters - absolute value of impedance ($|Z|$), absolute value of admittance ($|Y|$), Phase angle (θ), resistance (R), reactance (X), conductance (G), susceptance (B), inductance (L), capacitance (C), dissipation factor (D) and quality factor (Q).

The zero offset adjustment function measures the residual impedance and stray admittance inherent to the test fixture used, and offsets the effect of these parasitic parameters to zero with respect to the measured value [52].

5.2 Experimental Details

5.2.1 Absorption spectrum measurement

The chloroform solution of POPT with a concentration of 5mg/ml was prepared. The glass was cut to the required size and washed with distilled water and methanol. The glass was placed on the chunk of the spinner and the solution of POPT was dropped on it. Then spinner was made to rotate at a speed of 600 rpm yielding thin and uniform film of POPT on glass. The thickness of the film is approximated in between 200nm and 300nm.

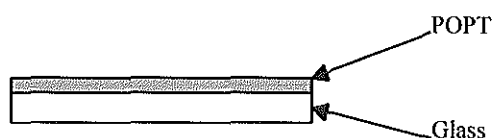


Fig. 5.1 A polymer on glass prepared for absorption spectrum experiment

The sample shown in the above figure was mounted on the sample holder of PERKIN ELMER $\lambda 19$ UV/Vis/NIR spectrometer. Using a PC with UVCSS the absorption spectrum was obtained (cf. Fig. 6.1).

5.2.2 *Current-Voltage measurement*

Our working sample has a sandwich structure of Al/POPT/ITO on glass. Generally there are two techniques of preparing such a sandwich device.

1. Vacuum evaporation technique and
2. Melt processing technique

Of these two techniques we have followed the first. Indium tin oxide (ITO) on glass was partly covered with photoresist. The exposed ITO was etched with a mixture of concentrated HCl, HNO₃ and water, 48:4:48 by volume. The etched part of the ITO/glass provided a convenient region for electrical contacts to the aluminum layer deposited later. The photoresist was removed using acetone, and then the surface was washed with methanol and distilled water. The POPT chloroform solution of concentration 5mg/ml was spin coated on the ITO/glass substrate at a speed of 600 rpm. The low work function metal (Al) was vacuum evaporated at a pressure of about 6.5×10^{-6} mb on POPT/ITO/glass structure to get our working sample, Al/POPT/ITO-glass sandwich structure shown in figure 5.2.

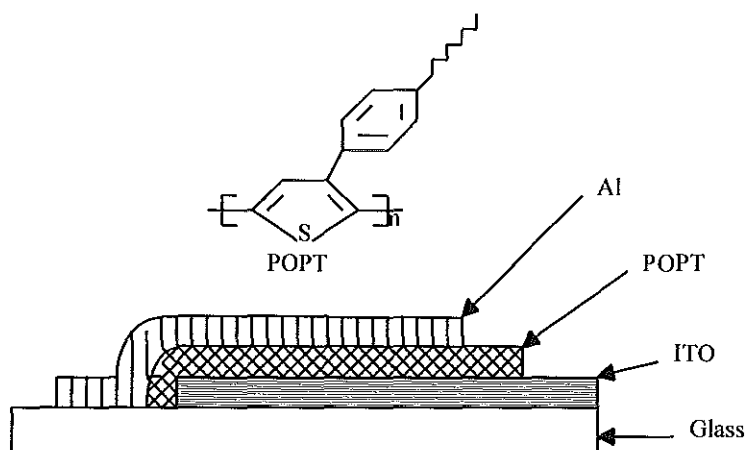


Fig.5.2 Schematics of Al/POPT/ITO sandwich structure.

Top: Chemical structure of POPT.

The area of the active junction of the structure was approximately 0.2cm x 0.5cm. The sandwich structure schematically shown in Fig.5.2 provides a means for current-voltage and complex impedance measurements. Current flows from the aluminum through the polymer film to the ITO, and the diode will be forward biased when the Al electrode is connected to the negative terminal of the voltage source.

The current versus voltage characteristic in the dark, at room temperature, was measured with an HP4140B pA meter/DC voltage source and an HP 16055A test fixture. The applied voltage was scanned between -3V and 3V (cf. Fig.6.2).

5.2.3 Complex Impedance measurement

The complex impedance as a function of frequency and applied voltage of the sandwich structure shown in fig.5.2 was measured using an HP 4192A LF Impedance Analyzer

with an HP 16047A test fixture. The complex impedance of the device was measured at a frequencies ranging from 500Hz to 10MHz for bias voltages ranging from -3V to 3V in steps of 1V. For every bias voltage, a sinusoidal oscillating voltage of $V_{rms}=10\text{mV}$ was used. The Cole-Cole plot of the device is given in Fig.6.3

6.2 Current-Voltage characteristics

Figure 6.2 (a) shows the J-V characteristics of Al/POPT/ITO device in the dark. The forward bias corresponds to the Al being negative. The J-V curve is asymmetric and non ohmic. The forward current increases exponentially at low forward voltage region. The device clearly exhibits rectifying behavior in the dark. The rectification ratio $\gamma = 3 \times 10^2$. A semilogarithmic plot (fig. 6.2 (b)) of the forward current density (J) versus the applied voltage (V) shows that the forward current increases exponentially in the applied voltage between 0.5V and 2V. This exponential dependence can be attributed to a formation of the depletion region between the Al and the polymer (see also section 6.3). According to the Schottky barrier theory [35], p-type semiconductors form a rectifying barrier at the interface when the work function of the metal is smaller than that of a semiconductor. However, if the interface is formed between p-type semiconductor and high work function metal (ITO), the junction gives an ohmic J-V characteristics (rather than rectifying). Since neutral POPT behaves as a p-type semiconductor [24], its work function is in between those of Al (4.2eV) and ITO (4.9eV), yielding a rectifying contact with Al.

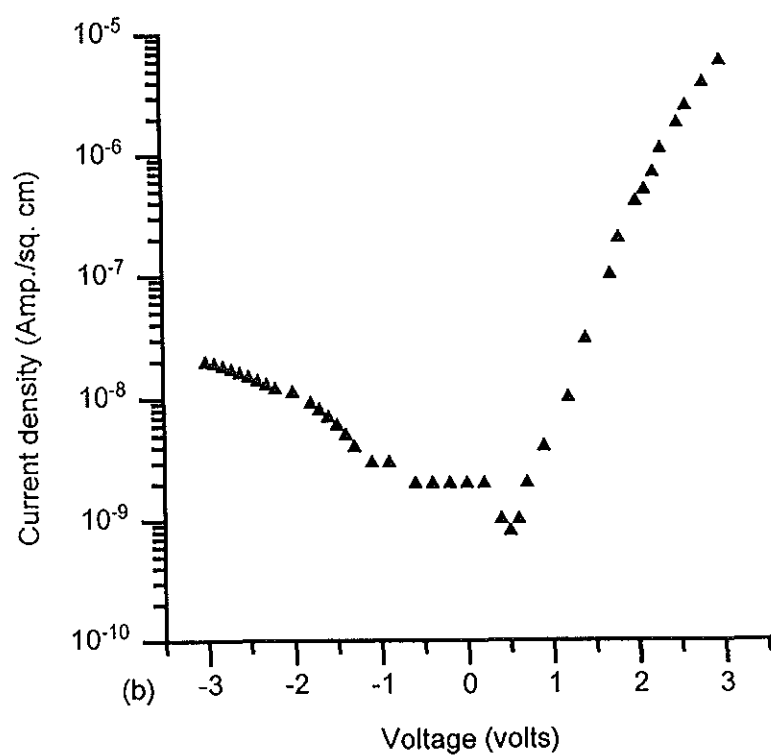
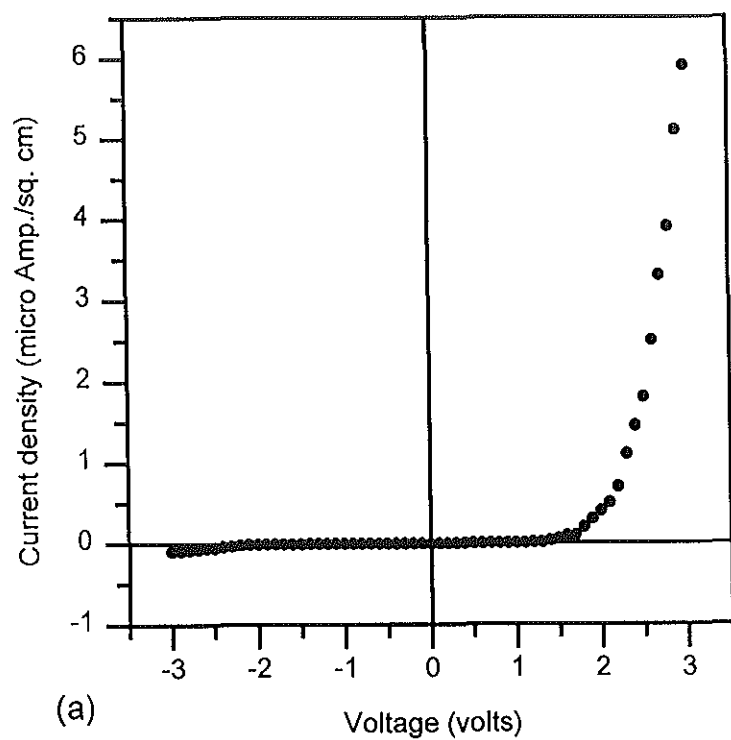


Fig. 6.2 a) Current density-Voltage characteristic of POPT.

b) Semi-log of J-V plot of POPT.

reported for PTOPT [24] that J_0 and n are 10^{-15} A/cm^2 and 1.2, respectively. So our results for the values of J_0 and n are quite large (cf. Table 6.1) relative to the indicated values of PTOPT. The large value of the saturation current density (J_0) results in large value of ideality factor (n), and this is an indication of current crowding, high probability of recombination of electrons and holes in the depletion region and occurrence of tunneling conduction [53,54].

Table 6.1 Parameters obtained from J-V plot and absorption spectrum.

J_0	ϕ_b	E_g	γ	n
10^{-10} A/cm^2	1.1 V	1.77 eV	3×10^2	4.27

6.3 The Cole-Cole plot

Figure 6.3 shows the impedance spectroscopy results for the sample as a function of frequency and applied voltage. The filled points are the measured coordinates of the real and imaginary parts of the impedance. The impedance spectra consist of part of single semicircles whose diameters correspond to the resistance of the depletion region for the corresponding bias voltage. These semicircles are bias voltage dependent. Smaller bias voltages give semicircles of larger diameter when extrapolated. This is consistent with the I-V curve of the device (cf. Fig.6.2)

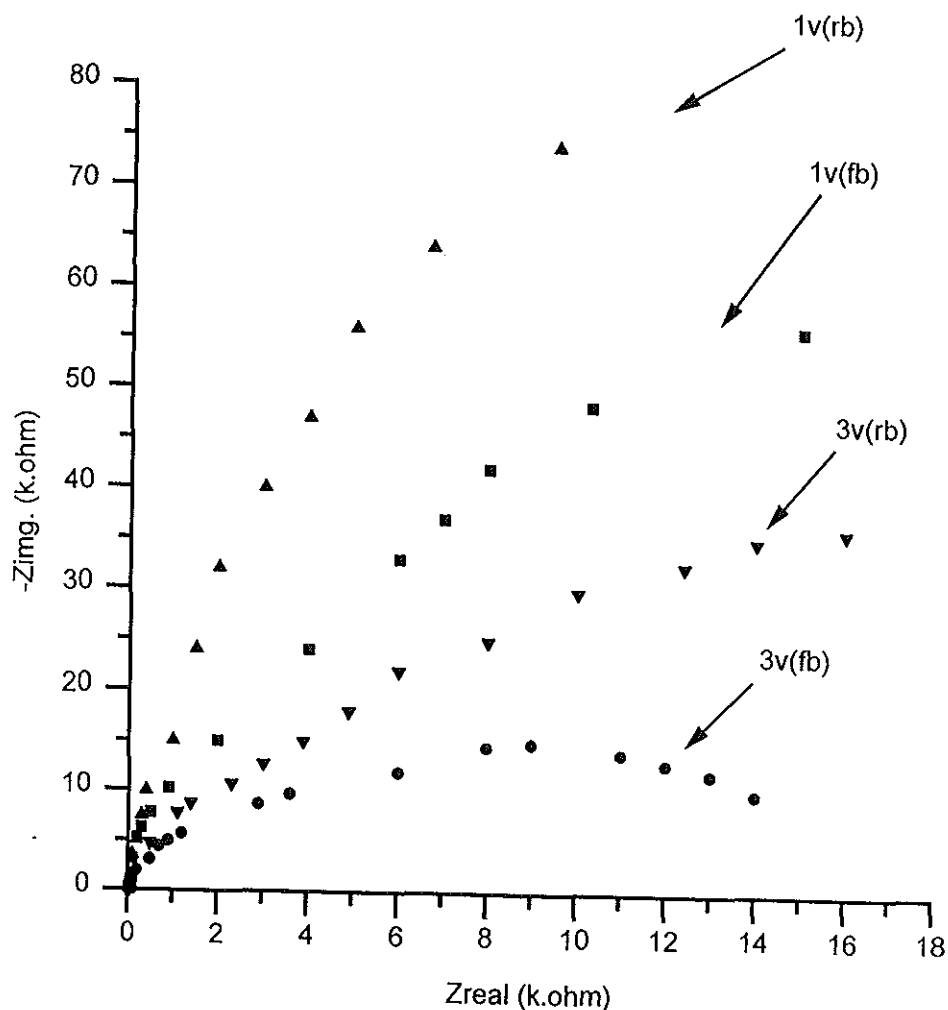


Fig. 6.3 Cole-Cole plot of Al/POPT/ITO sandwich structure.

Impedance spectroscopy yields an electrical equivalent circuit for the device. So we can model our sample (Al/POPT/ITO) by an equivalent electrical circuit given below.

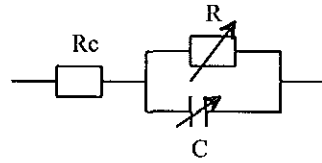


Fig.6.4 An equivalent circuit for Al/POPT/ITO structure as modeled for the Cole-Cole plot of fig.6.3. The arrows indicate that both R and C are bias voltage dependent.

An ideal Cole-Cole plot of the complex impedance is a semicircle with its center, the zero frequency and the infinite frequency intercepts on the Z_{real} axis [46]. This "depressed" single semicircle supports a model where a single barrier at the Al/POPT interface is dominating the charge transport through the diode. There is no evidence for a partially or completely overlapping second semicircle due to a barrier at the other electrode. Usually the zero frequency real impedance is obtained by extrapolating. The contact resistance, R_c , is the distance from the origin to the intersection of the semicircle with the real axis of the impedance plot corresponding to the highest frequency. The relation $-Z_{img} = (\omega C)^{-1}$ is used to estimate the value of the capacitance C. Knowing f ($\omega = 2\pi f$) and $-Z_{img}$ gives the value of C for the corresponding bias voltage. The parameters from the Cole-Cole plot are listed in Table 6.2.

Table 6.2 Parameters^a obtained from impedance spectra for Al/POPT/ITO device.

The negative values of V_b are reverse bias voltages.

$V_b(\text{V})$	$R_s(\text{ohm})$	$R(K.\text{ohm})$	$C(\text{nF/cm}^2)$
3	48	16	110
1	48	32	56
-1	48	44	50
-3	48	30	60

a. R_s and R are series and depletion region resistances, respectively.

7. Conclusion

In this research, we studied the electrical properties of an Al/POPT/ITO device prepared in our laboratory. The result of its absorption spectrum shows that the energy gap of POPT is 1.77eV. From the band theory of solids, a substance with this energy gap behaves as a semiconductor at room temperature [55], thus POPT is a semiconductor.

The current-voltage characteristic of the Al/POPT/ITO device manifests the properties of the Schottky barrier diode. For small forward voltages, the I-V characteristic of the device is governed by thermionic emission equation. However, for higher voltages the resistance of the depletion region decreases and ohmic behavior dominates. The thermionic emission model has been applied in order to interpret the I-V characteristics of the device. The values we found for the reverse saturation current density and the ideality factor indicate that the device is a leaky diode.

Al/POPT interface forms an insignificant (or no) interfacial insulating layer between the aluminum and the polymer as evidenced by complex impedance spectroscopy. The Cole-Cole plot shows part of a single depressed semicircle which is (fig. 6.3) bias voltage dependent. The absence of other overlapping semicircles indicate that Al/POPT junction can be viewed as a metal-semiconductor (MS) contact. It has also shown an increase of the resistance of the depletion layer at smaller magnitudes of the bias voltage. This is again a confirmation for the existence of tunneling conduction. Further studies are therefore necessary to get a diode with high rectification and better ideality factor from the polymer POPT. Particularly Al/C₆₀/POPT/ITO structure may significantly improve the electrical properties of the device.

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