OFET based sensor and Biosensor: Fabrication and Characterization in Advance Applications

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By

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ABBREVIATIONS

OFET- Organic Field Effect Transistors

TFT - Thin film transistor

CPs – Conducting Polymers

OMs- Organic Materials

ICs- Integrated Circuits

OLED -Organic Light-Emitting Diode

P3HT- Poly (3-Hexylthiophene)

PPV- Poly (P-Phenylenevinylene)

PFO- Polyfluorene

OPVs -Organic Photovoltaics

PECVD- Plasma Enhanced Chemical Vapor Deposition

CVD- Chemical Vapor Deposition

CMOS- Complementary Metal–Oxide–Semiconductor

PMMA- Poly (Methyl Methacrylate)

Vt- Threshold Voltage

EF- Fermi Energy Level

OSC-organic semiconductor

BGOFET- Bottom Gate Organic Field Effect Transistor

FESEM- Field Emission Scanning Electron Microscope

PANI -Polyaniline

DM -Dielectric Modulation

Title: OFET based sensor and Biosensor: Fabrication and Characterization in Advance Applications

ABSTRACT

The work focuses on new alternative or successor device which can counterfeit its disadvantages, share maximum benefits and extra, advantages over standard device. In this thesis we exploring devices like OFET and Biosensor for advance applications and determining their credibility as a future device. Recent advancements in the field of sensor technologies have resulted in low power, miniaturized, high speed and cost effective sensor.

The First device explored is an OFET device, so we have modelled and fabricate three independent structures of OFET: PPV based OFET, Pentacene based OFET and PANI based OFET for Humidity sensor. Our proposed structure exhibits, lower OFF current and good threshold voltage (V_{th}). Here we modeled and characterized and analyzed important parameters compared them with the fabricated device parameters. The results show that organic gate dielectrics possess potentially inexpensive alternative to inorganic counterparts and good electrical performance. Here we fabricate only two structures Pentacene based OFET and PANI based OFET. Polymers are the major class of materials for fabrication of humidity sensor. Using P-channel organic semiconductor i.e. polyaniline as an active layer and gate insulator Silicon dioxide (SiO2) layer on n-type silicon substrate, humidity sensor based on organic field-effect transistor (OFET) was created. This device is compatible with low power applications. In this thesis, a new method for developing realistic simulation models of Organic Field Effect Transistor (OFET) is presented. Further, the application of OFET in humidity sensor using P-type semiconductors acts as an active layer is investigated. PANI has been used in humidity sensor devices based on the electrical conductivity with water vapor. Humidity is a crucial ambient parameter which needs to be monitored for a wide range of applications such as instrumentation, automated systems, agriculture, and climatology. Organic polymer based material have been explored for the fabrication of humidity sensor. The application of humidity sensors in agriculture, are plantation protection, soil moisture monitoring. The FESEM (Field Emission Scanning Electron Microscopy)

have been presented to measure the roughness of the gate dielectrics influences the organic molecule growth.

In second work a Biosensor device is explored and used as fruit freshness detection. In this work, a highly sensitive, robust and cost-effective capacitive biosensor has been proposed and its applicability towards testing fruit freshness has been experimentally demonstrated. The fabricated TiO_2-based thin film sensors are incorporated with microgap cavities which when embedded into the fruit surface becomes sensitive to any dielectric (ϵ_k) changes that occur in the fruit during the phase of rotting. The sensors are hence based on the principle of dielectric modulation (DM). FESEM has been performed on the samples in order to visualize the surface changes in the microgap cavity. The proposed biosensor can be used as a low cost, portable sensing system as opposed to the existing bulky and expensive equipments that are presently used in determination of fruit freshness.

CHAPTER-1

Introduction and Organization of Thesis

1.1 Introduction:

The estimated end of Moore's Law deviates the industry to acclimatize to new and different architecture to continue the sizable processing of silicon industry. Our concern towards low power and high-speed devices with improved device density promote miniaturization, which facilitates nanoscale device dimensions with improved RF performance [1]. In order to satisfy these criteria α-Si TFTs endure drawbacks. Thus, we focus towards new alternative devices which can share maximum benefits, and advantages over standard α-Si TFTs [2],[3].

Over the past twenty years, the applications of organic semi conductors (OSCs) have intensive rapidly. Though their electron mobility is much lower than that of typical semiconductors, OSCs show promise in low-cost, flexible, lightweight, and environmentally-friendly semiconductor applications. Their hole mobility was found to be comparable to that of amorphous silicon (a-Si), with values exceeding 1.0 cm^2/Vs [4]. Their high hole mobility has led to p-type semiconductor applications in organic light emitting diodes (OLEDs), photovoltaic cells, and organic field effect transistors (OFETs). The progress in the synthesis and purification of organic semiconductors and the mobility of the best OFETs has exceeds that of α-Si TFTs. this thesis will focus solely on different OFETs [5].

First device a PPV Based Bottom Gate Organic Field Effect Transistor (BGOFET) is explored which has been a hiked in recent times. We used an organic semiconductor in its channel. One of the most widely studied organic semiconductor materials used for OFETs is PPV with 0.00001-0.0001cm^2/Vs carrier mobility. The proposed device also exhibits an excellent sub threshold swing (SS) 41mV/decade along with high ON current. in this paper better ON/OFF current ratio (10^{18}) and low ON voltage have been determined for this bottom gate OFET, which is based on poly (p-phenylenevinylene) (PPV or polyphenylene vinylene) $(C_8H_6)n$, and it is used here as p-type conducting polymer for the very first time [6].

Second device is Pentacene based OFET is explored. Among many organic materials, Pentacene is a p-type organic semiconductor material and the most prominent organic semiconductor material that has been widely used by other researcher in fabricating the organic devices. Pentacene based OFETs has a typical field effect mobility of around $10^{-5}cm^2/V.sec$. Therefore the carrier mobility of Pentacene devices is comparable with other α-Si devices. The device is operating in lower threshold voltage. In this paper, we propose a bottom gate OFET device composed of Pentacene as a conducting channel and SiO2 as an insulator that has high ON/OFF current ratio and low ON voltage which will be used as a humidity sensor and different gas sensors in further optimization. This device is compatible with low power applications. In this work, we only concentrate on simulation and fabrication of p-type OFET with top contact to evaluate and verify I-V characteristics In this thesis we fabricated a thin-film OFETs with Pentacene on a SiO2 gate dielectric followed by low-temperature aluminium deposition of the source-and- drain contacts. The FESEM (Field Emission Scanning Electron Microscopy) have been presented to measure the surface roughness [7].

The third work is to explore Fabrication of PANI based Organic Field-Effect for humidity sensor. Polyaniline (PANI) is a p-type organic semiconductor material and it has been studied for many applications including logic circuit components, electromagnetic shielding, chemical sensing and anticorrosion due to its easy synthesis, room temperature operation, and relative environment stability. Humidity sensors are useful for the detection of the relative humidity (RH) in various environments. PANI has been used in humidity sensor devices based on the electrical conductivity with water vapor. Polymers are the major class of materials for fabrication of humidity sensor. Using P-channel organic semiconductor i.e. polyaniline as an active layer and gate insulator Silicon dioxide (SiO2) layer on n-type silicon substrate, humidity sensor based on organic field-effect transistor (OFET) was created. This device is compatible with low power applications. In this work, we only concentrate on fabrication of conducting polymer OFET with top contact to evaluate the humidity and verify I-V characteristics. The p-type OFETs operating in an enhancement mode with the current saturation (I_{Sat}) was 0.8μA and the threshold voltage V_T was found to be 2.2V.The FESEM (Field Emission Scanning Electron Microscopy) have been presented. The results show that organic gate dielectrics possess potentially inexpensive alternative to inorganic counterparts and good electrical performance [8].

In the last work a Biosensor device is explored and used as fruit freshness detection. Nowadays there has been an increased demand for good quality, additive-free, nutritious and minimally processed food products. Health conscious consumers seek freshly-squeezed fruit juice that is sold under the label of 100% fresh fruit. These fruit juices are wholly made up of fresh fruits. After the fruits are harvested, natural metabolic activities and cellular respiration, causes change in the fruit quality such as firmness, pH, etc. Fruit freshness may be manually determined by the morphological characteristics (firmness and color). However, in bulk processing applications, manual determination of fruit freshness may not be feasible. In this work, a highly sensitive, robust and cost-effective capacitive biosensor has been proposed and its applicability towards testing fruit freshness has been experimentally demonstrated. In this paper we have proposed a thin film based capacitive biosensor for the determination of fruit freshness. The sensor uses capacitance as a sensing metric and provides a cost-effective, low power and high speed means for the determination of fruit freshness without the involvement of bulky equipment or expensive image processing systems. Capacitive biosensors fall under the category of impedance biosensors. Biosensors are devices that use sensitive materials or structures to recognize the presence of certain materials and provide information regarding those materials. The detection of bio-molecules by electronic means using various micro and nanostructures has attracted a great deal of attention over the past few decades [9].

1.2 Literature Survey and Background Research

1.2.1 Organic Field Effect Transistors (OFET)

Bardeen, Shockley and Brattain invented the world's first transistor in 1947.The first OFET was reported in 1986.Tsumura demonstrated an OFET with polythiophene in which a large modulated current was obtained. It was based on a film of electrochemically grown polythiophene. Polythiophene belongs to the family of conducting (or conjugated) polymers (CPs) that were discovered in the late 1970s.OFETs adopt the architecture of the thin film transistor (TFT), which has proven its adaptability with low conductivity materials, particularly in the case of amorphous hydrogenated silicon (a-Si:H). Then, OFETs using poly (3-hexylthiophene) as an active semiconductor were reported in 1988 [1], [2].

The application of organic electronics is used in the field of electronics displays, Sensors, radio frequency identification tags, Smart cards and organic solar cell that can be realized by use of the semiconducting properties of small molecules and polymers for cost-effective solution-based manufacturing techniques. Organic field-effect transistors (OFETs) are the basic building device for various microelectronic systems. As a result of extensive research efforts on molecular engineering, process development, and device optimization, recent reports show in both p- and n-type OFETs [3].

Since 1960s, the modern industry of microelectronics began to utilize the crystalline materials of simple elements, e.g. Si and Ge, or some compounds, e.g. InSb and GaAs, to make the basic devices for the integrated circuits (ICs). However, with the challenges arising from the considerable miniaturization, further development becomes more and more severe. On the other hand, many new materials and new technologies are emerging, such as nano wire, graphene and organic materials (OMs). In fact, the OMs have been studied from 1940s. Due to their poor electrical characteristics (high resistivity, low mobility) and the lack of understanding of transport mechanism, the progress in this domain remained relatively very slow. This situation lasted till 1986, the first appearance of organic transistor. Over the past few decade, organic field effect transistors (OFETs) have been established as electronic technologies due to their printability, low cost, and flexibility. The first thiophene-based OFET reported by Koezuka et al. In 1987 to fully printable plastic based OFETs. They have been achieved, such as very high mobility, low hysteresis, and steadily improving stability. The better understanding of the physics behind OFETS can enable tremendous improvement in OFET-based circuits. Organic and inorganic semiconductors have been used to integrate TFTs for more than 20 years. They exhibit better characteristics in comparison to amorphous silicon-based transistors due to the achieved performance and low production cost the combination of low-temperature processibility with the mechanical flexibility of organic materials leads to a wide range of applications in flexible electronics with a potential for very low cost manufacturing [10]-[12].

1.2.2 Biosensor-

The traditional methods used to determine the shelf life of fruits and vegetables use chemical, physical and microbiological metrics such as bacterial counts, phenolic compounds, color and texture for sensory evaluation. These aforesaid methods are time-consuming and require highly-skilled personnel to operate the equipments and interpret the results. To study the morphology of fruits several image processing techniques have been used. A. Gongal et al [13] used B/W camera, color camera and spectral camera to study fruit geometry and texture. They developed a system using these passive sensors for fruit detection and analysis. Czieczor et al developed a non-invasive method to determine the quality of pomegranate fruit. They used a luster sensor and a 3-D profilometer to measure the luster and surface roughness, respectively. Appreciable reduction in luster values and surface roughness (both mean roughness and roughness depth) of the pericarp was observed during the period of observation. These methods are infeasible in applications that require rapid diagnosis of samples. Sensory analysis methods are cost effective and are capable of providing comprehensive quality information. Electronic nose (E-nose) and electronic tongue (E-tongue) techniques have been developed to mimic the senses of olfaction and taste, respectively. The E-nose comprises of gas sensor arrays which interact with odor molecules to produce electrical signals. The responses from the sensor are fed into a computing system using multivariate data analysis methods. The information is used to construct a database and train a pattern recognition system so that the different odors can be identified and classified. An electronic tongue is an array of sensors that work on the liquid samples. The total response of the tongue sensor arrays vary from solution to solution owing to the presence of different compounds and ions in the sample. The senses of smell and taste are highly co-dependent. R. Banerjee (Roy) et al [14] used a combination of E-nose and E-tongue for the instrumental testing of tea. They used radial basis function neural network to report an increased classification rate of 93% for the combined E-nose and E-tongue system, whereas the individual classification rates are 83-84% for E-nose and 85-86% for E-tongue, respectively. H-Z Chen et al evaluated the freshness of fresh cut green bell pepper using E-nose and established this type of sensory system is suitable for monitoring the freshness of fruits and vegetables [15]-[18]. S. Kiani et al used the electronic nose system for assessing the quality of medicinal and aromatic plant products. They showed that quality indicators such as aroma, taste and color could be used to design a robust system for real-time monitoring of product quality. M.A.K.P. Tolentino et al developed a piezoelectric sensor to monitor the ageing of fruits during the post harvest period. Ethylene is known to play a key role in the ripening of fruits. The presence of atmospheric ethylene may have adverse effects on the shelf life of fruits. The sensor used a quartz crystal microbalance (QCM) and showed that the oscillating frequency of the QCM decreased in the presence of ethylene. The development of biosensors began in 1950, when L. L. Clark develops biosensors with an oxygen electrode (Clark electrode) in Cincinnati, USA to measure the dissolved oxygen in blood. Later Professor Leland C Clark, "Father of Biosensor" who described the first enzyme electrode was reported in 1962. Lubbers and Opitz (1975) described a fibre-optic sensor with immobilised indicator to measure carbon dioxide or oxygen. The term biosensor is coined by Cammann in 1977. In 1987, a pen-sized meter for home blood-glucose monitoring formed the basis for the screen-printed enzyme electrodes launched by MediSense (Cambridge, USA). Biosensor consists of two components, a biological element which usually an enzyme detects the biological element, a transducer i.e. an electrode which converts the biological event into an electrical signal. A variety of bio recognition element ranging from enzyme to antibodies is available for use. This information conveys the fundamental of biosensor for the development and optimization of a biosensor [19]. In recent few years there has been an increased demand for high-speed, highly sensitive, cost effective and accurate sensors for the analysis and detection of chemical and biological analytes. A biosensor must be capable of providing rapid, real-time and reliable information regarding the biomolecule under study. Biosensors are also used in clinical diagnostics, environment monitoring, drug detection and food analysis. The advantages of biosensors include low cost, small size, quick and easy use, as well as a sensitivity and selectivity greater than the others [20]-[23].

1.3 Organization of the thesis:-

Chapter-1

This chapter includes introduction of the thesis which includes objective and motivation of the thesis. Followed by the introduction of four device sensors explored in this thesis- PPV based OFET, Fabrication of OFET using Pentacene, PANI based OFET fabrication for humidity sensor and TiO_2 based thin film capacitive Biosensor towards fruit freshness detection.

Chapter-2

This chapter is illustrated the Organic Field Effect Transistor with device modeling, architecture, characterization and fabrication of devices. Comparative study of organic semiconductor, application of organic semiconductor is elaborated.

Chapter-3

The chapter illustrates the PPV based bottom gate OFET device, so we have to model the device to realize the I-V characteristics and important parameters are evaluated for the proposed structure.

Chapter-4

The chapter illustrates Pentacene based OFET. We have modelled and fabricated the structure. Our proposed structure exhibits an excellent threshold voltage better ON/OFF current ratio. Finally we compare important parameters of simulated and fabricated device. The FESEM (Field Emission Scanning Electron Microscopy) have been presented.

Chapter-5

The chapter illustrates PANI based OFET for humidity sensor. We have modelled and fabricated the structure. Our proposed structure exhibits an excellent threshold voltage. PANI has been used in humidity sensor devices based on the electrical conductivity with water vapor. Finally important parameters of fabricated device are evaluated. The FESEM (Field Emission Scanning Electron Microscopy) have been presented.

Chapter-6

In this Chapter a thin film based capacitive biosensor for the determination of fruit freshness is illustrated. Capacitance versus No. Of days plot of three different fruits samples results are elaborated. FESEM has been performed on the samples in order to visualize the surface changes in the microgap cavity.

Chapter-7

This concludes the thesis outcomes and future scope of the OFET based sensor and Biosensor and their fabrication and characterization.

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Chapter-2 Introduction to OFET

2.1. Organic Semiconductor:-

The various materials can be categorized according to their electrical properties as conductors, semiconductors and insulators. Resistivity r and its reciprocal conductivity s are the most important electrical properties. It is well known that materials are comprised of atoms. Each atom has a nucleus and electrons revolving around it and nucleus consists of protons and neutrons. The attractive force between the positive charged protons and the negative charged electrons are responsible for holding this structure together. According to Niels Bohr, electrons exist in the specific orbits or shells around the nucleus, the outermost of which is called a valence shell. They can transit to a shell of higher (or lower) energy level by absorbing (or losing) energy, equal to the difference of the two levels. This energy has the form of a photon or heat. Free electrons have higher energies and are said to exist in the conduction band. Electrons not freed from their atoms have lower energies and are said to exist in the valence band. Energies between the conduction and the valence bands form the band gap Eg. Electrons can exist in the conduction or the valence band, but not in the band-gap [1]- [3].

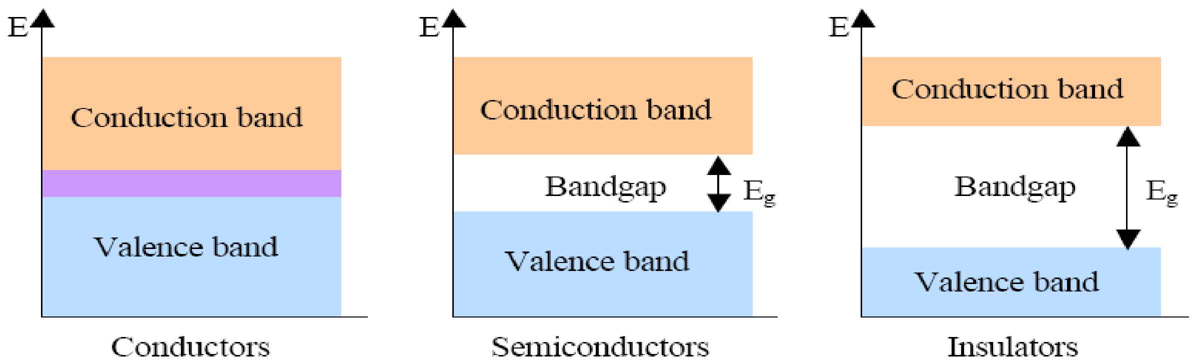

Fig: 2.1 Energy bands in various material types.

In conductors, the conduction and the valence bands overlap, thus there is no bandgap, as illustrated in Figure 2.1. For this reason, electrons can move from one band to the other. Finally, Eg tends to decrease with temperature. The number of free electrons, and thus conductivity, can be increased by offering amounts of energy to them at least equal to the bandgap. Obviously conductors do not require any such energy. On the contrary, in order to reach noticeable conductivity levels, insulators require large amounts due to their large Eg. Semiconductors with much less energy reach levels almost as good as conductors. While electrical systems use exclusively conductors and insulators, electronic systems are entirely based on semiconductors. That is because of their unique ability to behave as conductors and as insulators according to our needs. All diodes, transistors and thyristors are built using semiconductive materials. The most common semiconductors are silicon (Si) and Germanium (Ge). Those are also called group IV materials due to the numbers of valence electrons. Inorganic semiconductors like Si and Ge became the backbone of the electronics industry after the successful demonstration of the field effect in 1947 by Bell Laboratries [4].

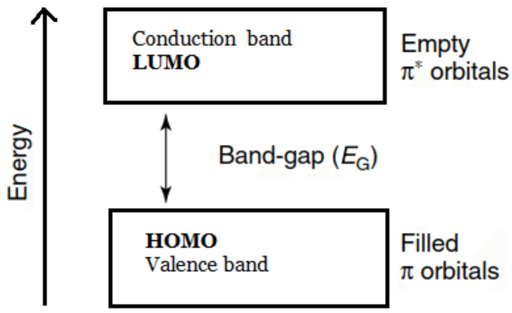

Fig 2.2 - Energy diagram of Organic semiconductor

As mentioned earlier, electrostatic forces of neighboring atoms attract electrons and form ions, in their attempt to reach chemical stability. Electrostatic forces among these ions form symmetric lattices that are called crystals. One of the simplest crystals is that of O2 and Ga, producing a simple *cubic* structure. Si and Ge form a more complex crystal called cubic face centered as shown in Figure 2.3 Each crystal structure is defined by a number called lattice constant a.

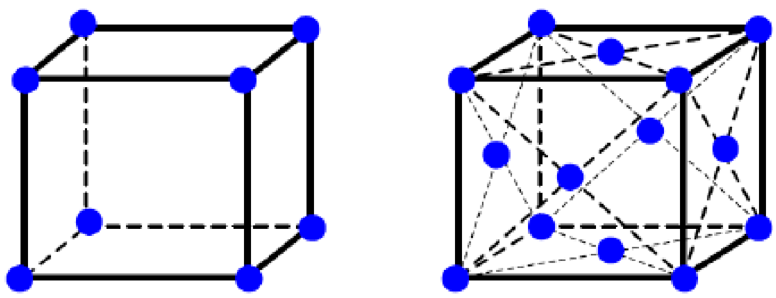

Fig.2.3. Examples of crystal structures

Production of crystalline materials in large sizes can be very expensive. Materials composed of very small crystals or grains are called polycrystalline. These have inferior properties than crystalline, but are much cheaper to produce. Materials with no crystal uniformity are called amorphous and their properties are far inferior, but they are very cheap. Organic semiconductor molecules have conjugated structures with single and double bonds of carbon-carbon bonds. The molecules have π-orbitals delocalized along the face of a molecule. This orbital delocalization allows electrons to move within a molecule. Organic semiconductors are structurally and chemically quite different from inorganic semiconductors. Inorganic semiconductors consist of atoms that are covalently or ionically bonded. The strong interaction between atoms by covalent boding leads to the delocalization of the individual orbitals of atoms. The interaction between orbitals creates more energy states and forms a quasi-continuous band in which the energy difference between individual energy levels is very small. In organic semiconductors, molecules are connected to each other by comparatively weak van der waals interactions. Therefore, electrons are largely localized to individual molecules except electrons in the π orbital, and the weak intermolecular interactions cause a narrow electronic bandwidth in molecular solids. As the interaction between π orbitals increases the degree of π-π overlap increases. This condition is favorable for the formation of energy bands. Due to the narrow bandwidth arising from the weak interactions between molecules in organic semiconductors the mobilities of charge carriers are low in organic semiconductors, with typical values of 10^{-2} cm^2/Vs, in comparison with values of 100-1000 cm^2/Vs or more in inorganic semiconductors.

In the past decades, organic semiconductors were used for the optical devices. The recent progresses made in the material engineering and fabrication technologies permit to improve the carrier transport properties in the organic devices, such as organic light-emitting diode (OLED), organic solar cells and organic field-effect transistors (OFETs). For a better understanding, we need to study the transport properties of organic semiconductors [5].

2.1.1 CARRIER TRANSPORT:-

If there is a higher concentration of carriers in a part of a doped semiconductor, then those carriers will tend to diffuse, spreading evenly all over the material. This is analogous to a gas expanding evenly in a container. The current produced by this movement of carriers is called diffusion current (I_D) and is analogous to the majority carrier concentration and thus the doping. The carriers (holes) shown in the following example (Figure 2.4) move to the right, where their concentration is smaller, producing I_D. Note that if the carriers displayed were electrons, I_D would be reversed. Current can also be produced by the movement of carriers by an external force, like an electric or a magnetic field. This will produce a current called *drift current* (I_S) and is analogous to the minority carrier concentration and thus the temperature. *Drift current* (I_S) is proportional to the intensity of the field. Again in the following example (Figure 2.5) the carriers displayed are holes [6].

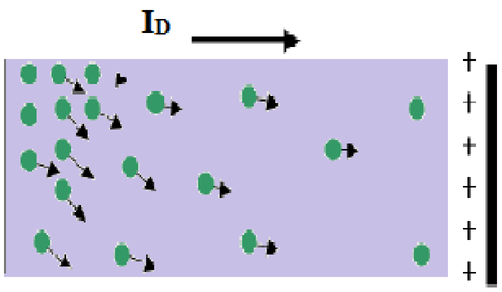

Fig 2.4 Diffusion Current

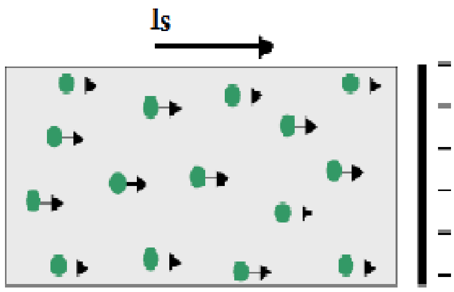

Fig 2.5 Drift Current

2.2 ORGANIC SEMICONDUCTOR MATERIALS:-

Organic semiconductor can be widely divided in two categories. Small organic molecules (e.g. Pentacene) have Low molecular weight and polymers (e.g. P3HT, PANI) with higher molecular weight. Organic semiconductors with low molecular weights can be thermally evaporated and have better crystallinity than polymers. The weak overlap between molecular orbitals in polymers and semiconductors leads to lower mobility than in small molecule semiconductors. Chemical structures of some of the common organic semiconductors are illustrated in Figure 2.2. Poly (3-Hexylthiophene) P3HT has been used in organic photovoltaic and it has a carrier mobility range of 0.01-0.1cm^2/Vs. Poly (p-phenylenevinylene) (PPV), Polyfluorene (PFO) are widely used in OLEDs and their carrier mobility ranges are 0.00001-0.0001 and 0.001-0.01 cm^2/Vs. The linear acene molecules (e.g. Pentacene, tetracene) are made up of fused benzene rings shown in figure 2.6.

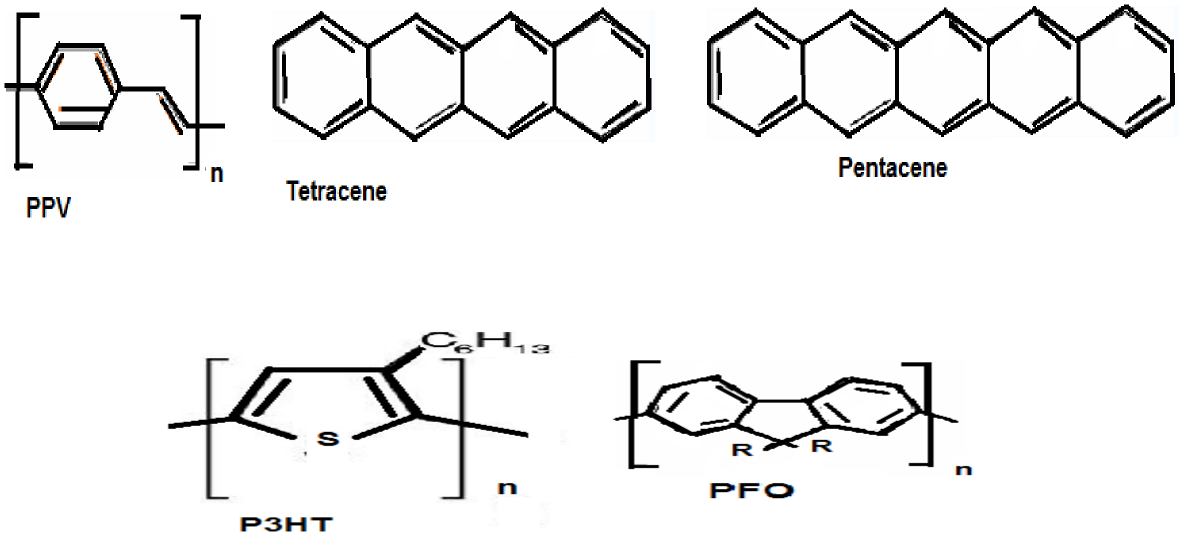

Figure 2.6 Chemical structures of organic semiconductors.

These molecules easily form relatively high quality semiconducting crystals. The acene molecules have sp^2 hybridized carbons in which carbon is bonded by σ bonds to its neighbors.2S, 2px and 2py orbitals of a carbon atom are hybridized and form the three σ bonds. The remaining 2pz orbital contributes to the formation of a π bond. The delocalization of electrons occurs through the overlap between π orbitals along the molecular chains within a molecule. Having different charge carriers, the organic semiconductor can function either as p-type or n-type.

In p-type semiconductors the majority carriers are holes, while inn-type semiconductors, the majority carriers are electrons. Accordingly, the transistors are p-type transistors or n-type transistors. The concept of hole and electron transporting materials are used to develop of organic light-emitting diodes, which seems more relevant for organic semiconductors [7]-[9]. N-Type and p-type materials are characterized by their low ionization potential and high electron affinity. Generally most of the organic semiconductors are p-type in their non doped form. This is mainly because p-type semiconductors are stable in air and have relatively high mobility when they are used in OFETs. Unlike p-type semiconductors, n-type semiconductors are sensitive to air and moisture, due to the organic anions, in particular carbanions. Moreover, the n-type semiconductors have low field-effect mobilities. But in organic electronics, n-type semiconductors are important components [10].

2.3 Organic / Inorganic interfaces in organic electronics:-

Organic electronics have been studied for application in electronics displays, Smart cards, RFID tags, Sensors and organic solar cell. It can be realized by the basic operation of organic electronic devices and the physics of organic semiconductor. Interfaces in organic electronic devices are organic field effect transistors (OFETs), organic photovoltaics (OPVs) and organic light emitting diodes (OLEDs). It takes important part in charge injection and transfer for operating devices. To determining power conversion efficiency in OPVs, Photo induced charge transfer between electron acceptor and donor layers is critical. In these devices, the absorption of light produces excitons in the electron donor layer that are subsequently dissociated at the interface. An intimate contact between donor materials with a low ionization potential and acceptor materials with a high electron affinity is required for efficient charge transfer at the interface [11]-[13].

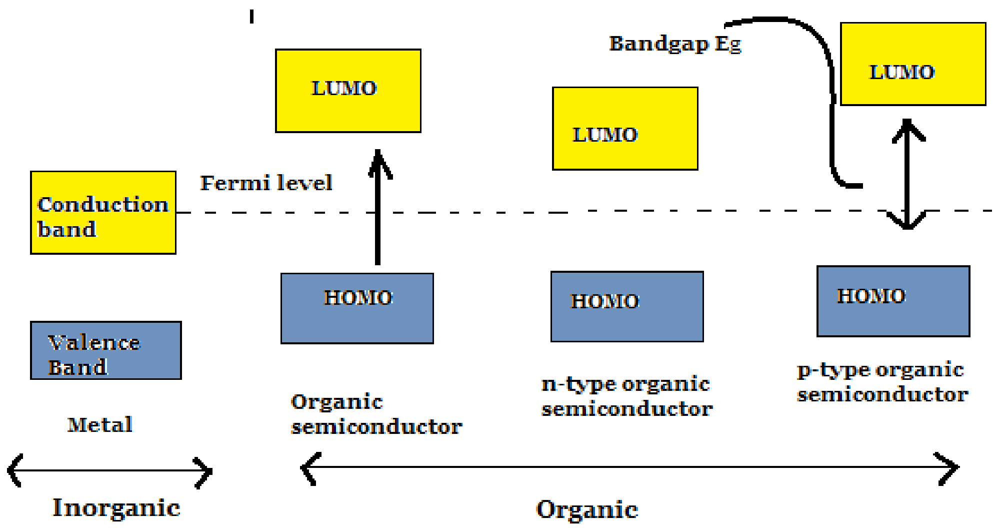

Fig 2.7 - Energy band diagram of metal, insulator and an organic semiconductor.

In OFETs, charge injection between the organic semiconductor and the metal electrodes and charge transport along with the interface between gate dielectric and organic layers are the most important in the operations of devices. The changes of contact resistance between the metal electrodes and organic semiconductors, depends on metal electrodes. In order to achieve efficient charge injection we required p-type organic semiconductor, metal electrodes with high work function. For efficient electron injection, metal electrodes with low work function are required.

The contact resistance between metal electrodes and organic semiconductors can affect the mobility of charge carriers in OFETs. In organic semiconductors, the gate dielectric can take important part in transport carriers. The charge carriers are induced near the gate dielectric when an electric field is applied to the gate dielectric. The device parameters such as threshold voltage and on/off ratio are changed by the result of interface between organic semiconductors and the gate dielectric. The roughness of the gate dielectric can also change the morphology of the organic film. The gate dielectric can produce valleys in the electrical channel between source and drain electrodes with increased of roughness of the gate dielectric, which is noisome for transport of carriers at the interface between the organic layer and the gate dielectric [14].

2.3.1 OFETs vs. Inorganic Thin-Film Transistors:-

OFETs, thin-film transistors (TFTs) are a Field Effect Transistor where we used an organic semiconductor in its channel acts as active layers. These are of great interest as a potential alternative to amorphous Si TFTs. The progress in the synthesis and purification of organic semiconductors and the mobility of the best OFETs has exceeds that of α-Si TFTs.

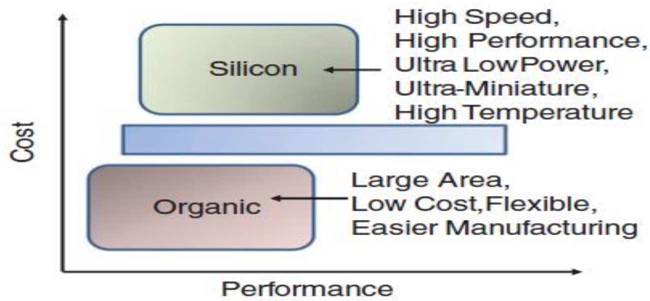

Figure: 2 .8 Cost versus performance of organic and inorganic semiconductors.

A major advantage of OFETs vs. α-Si TFTs is their compatibility with low-cost, low-temperature processes. A typical α -Si: H TFT fabrication process involves the deposition of hydrogenated α -Si as an active layer and silicon nitride as a gate dielectric by plasma enhanced chemical vapor deposition (PECVD) using H_2/SiH_4 (silane) andNH_3/SiH_4, respectively. The process temperature took usually much higher than 250 °C. On other hand, OFETS can be processed at lower temperatures using various simple, low cost techniques, including vacuum thermal evaporation, spin-coating, dip-coating, vapor deposition. Thus the combination of low-temperature processibility with the mechanical flexibility of organic materials leads to a wide range of applications in flexible electronics with a potential for very low cost manufacturing.

Secondly, α-Si technology provides only high performance n-channel transport which prevents the use of complementary metal–oxide–semiconductor (CMOS) technologies. In contrast, the versatility of synthetic organic chemistry has enabled the tailoring and engineering of both n- and p-type semiconductors, giving rise to many potential candidates for circuit designs based on CMOS technology [15]-[17].

2.4 Application of Organic Devices:-

Large-scale integrated circuits:

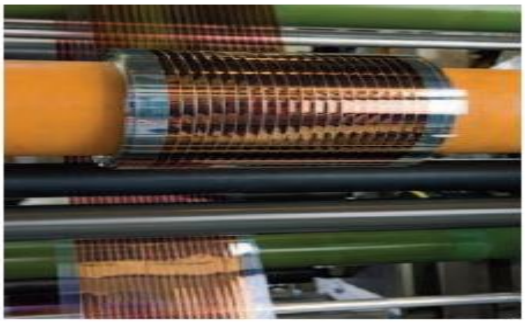

Fig2.9 - Roll-to-roll production of flexible organic photovoltaic modules.

Flexible display-

Fig2.10 -Full-HD OLED TV with thickness as small as 1cm.

□**Sensor and scanner:**

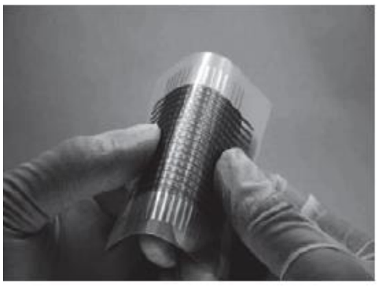 

Fig2.11 - left: A flexible, large-area pressure sensor. Organic transistors active matrix is formed on a plastic film and integrated with pressure-sensitive rubber. Right: An image of electronic artificial skin attached on the robot surface.

☐**RFID tags**: The organic RFID tags have shown much greater advantages compared to the currently used code bar for the domains of retail and logistics because of their very low cost, flexibility, good robustness.

Fig 2.12- RFID tags

☐**Solar cells:** The present solar cells are generally based on the polycrystalline silicon. Their high price obstructs the large-scale application.

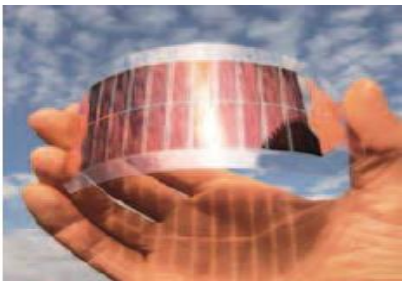

Fig 2.13 -Organic photovoltaic cell

2.5 Organic Field Effect Transistor (OFET)

Bardeen, Shockley and Brattain invented the world's first transistor in 1947.The first OFET was reported in 1986.Tsumura demonstrated an OFET with polythiophene in which a large modulated current was obtained. It was based on a film of electrochemically grown polythiophene. In the late 1970s, Polythiophene were discovered that belongs to conducting polymers (CPs) family. OFETs adopt the architecture of the thin film transistor (TFT), which has low conductivity materials, particularly in the case of amorphous hydrogenated silicon (a-Si:H). Then, OFETs using poly (3-hexylthiophene) as an active semiconductor were reported in 1988 [18].

Most of these early OFETs were fabricated using thin films of polymeric semiconductors formed from solution by spin coating, screen printing or inject printing. The polymer films are typically amorphous, and the carrier mobility is rather low, ranging from 10^{-5} to10^{-4} cm^2/Vs. OFETs are composed of three terminals, gate, source and drain. It can be shown that a sandwich structure consisting of a capacitor with one plate as the gate and the other plate as the semiconductor layer. The semiconductor layer is electrically interfaced with the other two electrodes. Figure 2.14 illustrates the basic schematic of an OFET. The Gate electrode is made up of conductive material such as highly doped silicon or gold, platinum that serves the purpose of the structural base for the device and of the conductive gate terminal. Generally silicon dioxide is preferred as the dielectric material. Polystyrene, parylene and poly (methyl methacrylate) (PMMA) are used as insulating polymers for making flexible devices. A gate dielectric layer separates the gate electrode from the organic semiconductor layer [19].

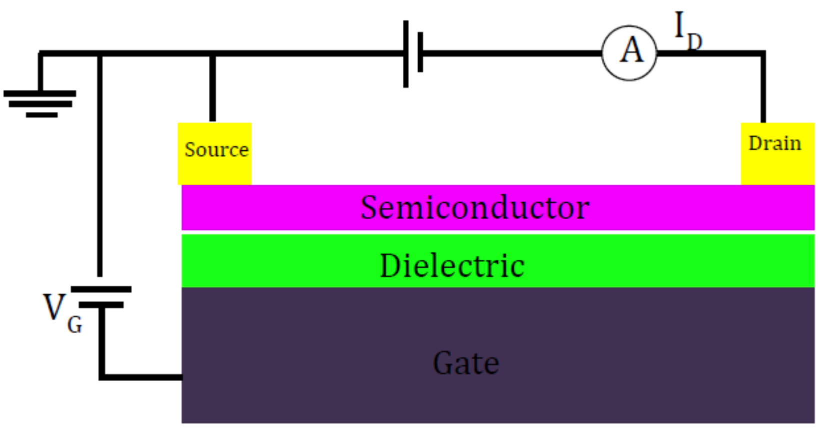

Fig 2.14 General schematic of an organic field effect transistor

2.5.1 OFET ARCHITECTURES:-

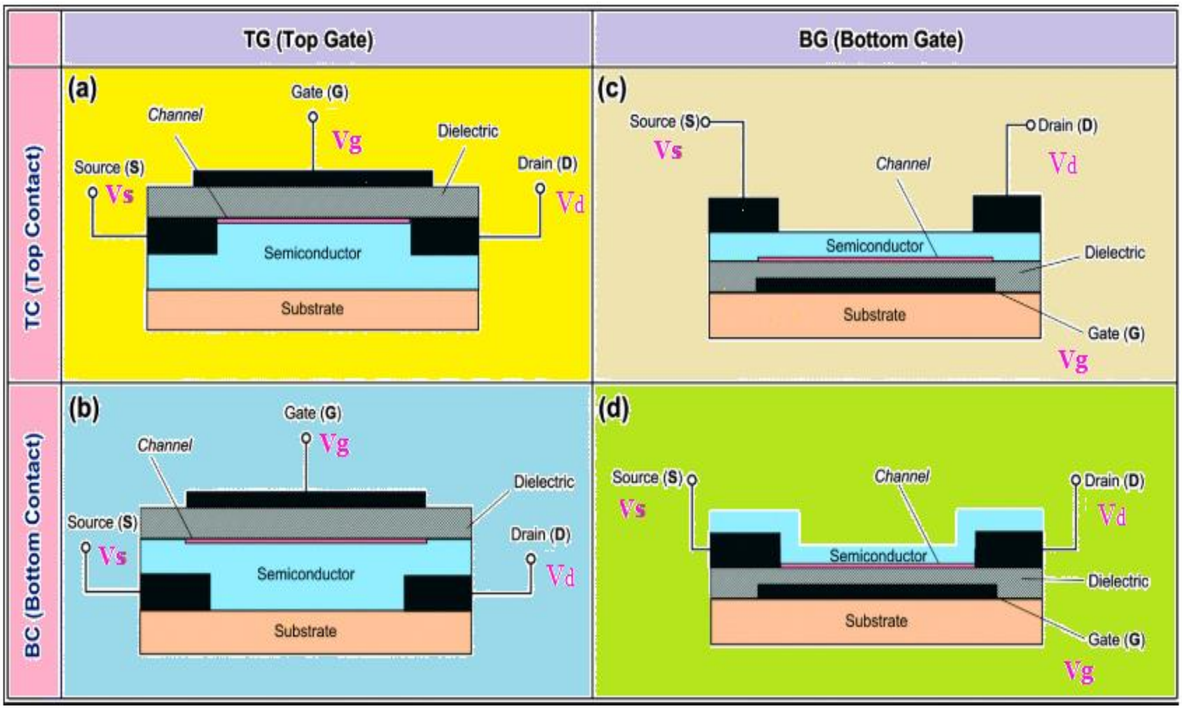

Figure 2.15 Section schematic diagrams of four configurations of organic transistors. (a) and (b) are top-gate (TG) configured, with top-contact(TC) and bottom-contact (BC) categorized source and drain electrodes, respectively. (c) and (d) are bottom-gate (BG) configured, with TC and BC source/drain electrodes, respectively.

Based on the position of the contacts (i.e., gate, source, and drain) OTFT can be categorized into four basic structures as shown in Fig. 2.15.Organic semiconductor is deposited onto the gate insulator and source/drain contacts for bottom-contact OFET devices, as shown in fig 2.15 (b) and (d). In top-contact OFET devices, the source/drain contacts are usually deposited on the organic semiconductor through a shadow mask that is shown in fig.2.15 (a) and (c).

With regard to TG/BG configuration, if the substrate is the BG the OFETs with such a common gate electrode will be easy to fabricate. For TG devices, because the gate insulator is deposited over the OSC film, the insulator should be easy to be dissolved in the solvents and does not degrade the nether OSC film. Therefore, the TG OFETs often suffer from the OSC/dielectric interface roughness and high "off" current, which may arise from the oxygen doping during the deposition of insulator on the OSC film. Another disadvantage on TG devices is the misalignment: the top-gate should accurately and completely cover the entire channel length defined by S/D. If a misalignment or ungated gap in S/D occurs, additional resistance will be introduced, resulting in higher contact resistance. Electrical performance of OFET devices with a top-gate structure can be significantly degraded during the deposition process of the top electrodes, and the film growth can be disturbed at the interface of organic semiconductor/metal contacts. The top contact configuration demonstrates better performance in comparison to the bottom contact due to less morphological disorders in the active layer. Additionally, the bottom contact structure demonstrates a higher sub- threshold slope in comparison to the top contact due to formation of a low mobility region near the contacts [20].

The bottom contact structures are promising for cost-effective flexible electronic applications, since it can be fabricated through simple printing techniques that make them highly suitable for large area display applications.

2.5.2 Parameters of ORGANIC OFET:-

Carrier mobility is proportional to semiconductor conductivity, and thus it is related to the performance of the device. Mobilities in the range of 0.1 to 1.0 cm^2/Vs are considered fairly well.

On/off current ratio is the ratio of the saturation current when V_{GS} is high to the leakage current when V_{GS} is zero. This ratio is used as the switching behavior of OFETs.

Threshold Voltage- The threshold voltage V_T of OTFTs varies with either the gate insulator capacitance or the thickness of the organic film .The devices with shorter channel length tend to have smaller threshold voltages . Lower V_T is useful in low power consumption devices.

Sub-threshold slope- The applied gate voltage is lower than threshold voltage, OFETs work in a subthreshold region and the sub-threshold slope is defined as:

$$SS = \frac{dV_G}{d(\log I_D)} = \frac{KT}{q}\ln 10(\frac{C_i + C_D + C_{ss}}{C_i})$$

where (kT/q) is the thermal voltage, C_D and C_{SS} are the depletion capacitance and the surface states capacitance, respectively. This SS is generally measured at the maximum slope of log (I_D) versus V_G, and it describes how the switch turns on and off in the subthreshold region.

2.5.3 OFET Device Operation:-

An OFET generally operates in the accumulation region as organic semiconductors have a very low intrinsic conductivity and the film is generally not doped intentionally. Source and drain electrodes are used to inject and collect charges from the semiconductor layer.

A minimum nonzero gate voltage called threshold voltage (Vt) needs to be applied before a conduction channel can be formed. When a gate voltage Vg-Vt>0 is applied a conductive channel is formed at the interface with charges opposite in polarity to Vg applied. Electric field is applied between the gate and the organic semiconductors attract charge carriers into a very thin sheet of charge at the interface between the organic semiconductor and the gate dielectric. A negative voltage is applied to the gate that increases the fermi energy level (E_F) and this leads to energy band bending at the interface between the organic semiconductor and the gate dielectric. E_C, E_V and Ei represent conduction band, valence band edge and intrinsic energy level, respectively [21].

- **Accumulation mode (VG<0V):**

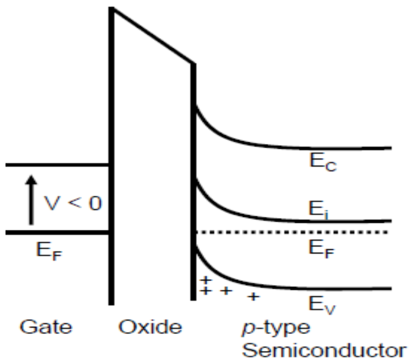

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Figure 2.16 OFET operations in accumulation mode

If a negative V_G is applied, in case of the n-channel transistor the negative gate voltage attracts holes existing in the p-type substrate to the insulator interface. Similarly in the case of the p-channel transistor the positive gate voltage attracts electrons to the insulator interface. In the accumulation mode the transistor stays in the off state. Suppose the gate electrical field attracts the majority carriers (here holes for the p-type doped silicon bulk) from the substrate bulk to the semiconductor/oxide interface. Hence the concentration of hole is significantly increased and the bands of Si bulk are bent close to the gate dielectric. Figure 2.16 has shown the OFET operation in accumulation mode.

When the source-drain voltage is comparable to the gate voltage the channel region near the drain contact begins to be depleted. At this point the voltage difference between gate and drain is equal to threshold voltage, V_t, and the conducting channel is said to be pinched off. In this case the drain current is given by

$$I_{Dsat} = \frac{W}{2L} C_i \mu (V_g - V_t)^2 \, , V_D > V_g - V_t$$

Where

I_d= Drain current

W= width of the channel

L= Length of the channel

Ci= Capacitance of the insulating layer.

μ= mobility

Vg= Gate voltage

Vt = Threshold voltage

Vd =Drain voltage

Transistors operate in the linear regime when the difference between the gate voltage and threshold voltage is much larger than the source-drain voltage. In this regime, I_{Dlin} increases linearly with V_g according to:

$$I_{Dlin} = \frac{W}{L} C_i \mu (V_g - V_t).V_D$$

In the linear regime, the conductivity of carriers induced in the channel depends on the charge concentration and the mobility according to the equation.

$$\sigma_{\square} = \frac{1}{R_S} = ne\mu$$

Here, $\sigma_{\square}$ is sheet conductance and n represents two dimensional density of charge carriers. R_s is sheet resistance. In the linear regime, when $Vg>V_t$, the charge carriers induced are mobile and the density can be expressed as:

$$n = \frac{Ci(V_g - V_t)}{e}$$

In the linear regime, mobility, μ, can be expressed by:

$$\mu = \frac{\frac{1}{R_s}}{ne} = \frac{1}{C_i}\frac{d\frac{1}{R_s}}{dV_g}$$

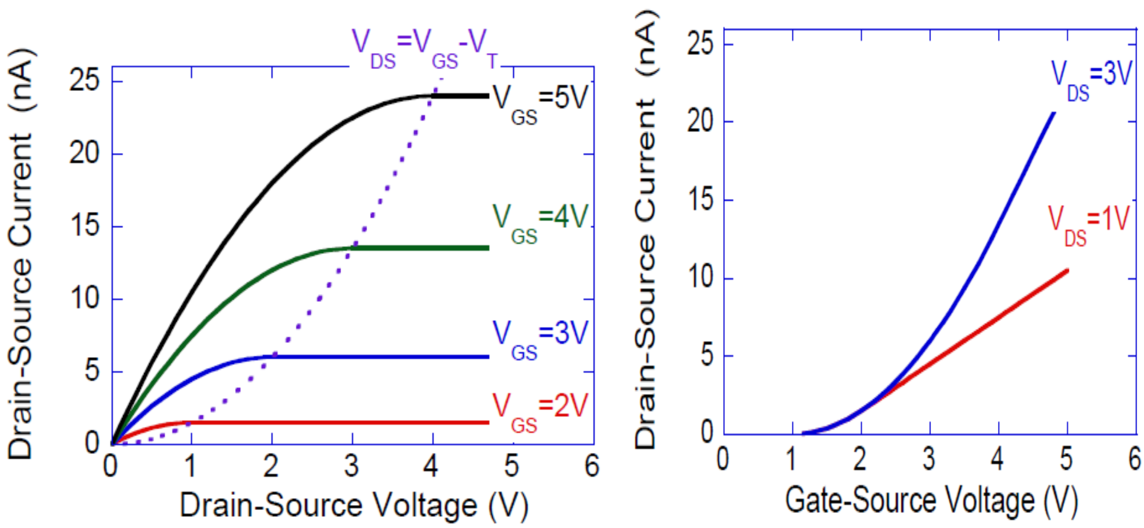


Fig 2.17- (a) Output characteristics and (b) transfer characteristics top contact OFET device.

In the output curves (a) as the Vds is increases for a given Vgs, the source–drain current at first increases linearly with Vds, and then saturates. In the transfer curves, the magnitude of Vgs is increases for a given Vds, the source–drain current at first increases quadratically with Vgs beyond a threshold voltage. When Vgs>Vds region, the linear-region field-effect mobility can be evaluated using a standard equation from silicon MOSFET theory.

2.6 Simulation OF OFET:-

The existing modeling and analysis tools, along with related publications, the suite of tools and reusable models were developed by Silvaco. In this chapter, the strategy and methodology, for modeling OFET using Silvaco, is discussed. An overview is also given of the software that was developed or reused in order to enhance its functionality and to meet the modeling and simulation needs for researching advanced OFETs devices.

2.6.1 MODELING TRENDS IN OFETs

There are a very large number of publications available that document the modeling of almost every aspect of OFET function and behavior. These span from the macroscopic electrical to the microscopic molecular level and have very high accuracy and credibility. Thus, there is a need to select and use a large number of different models, in order to study an actual complete structure. An important consideration is the fact that not all of these models are compatible with each other. This makes their selection prone to errors, quite hard, and time consuming. In addition, each one exposes the researcher to many detailed parameters that usually create a lot of unnecessary confusion. As a consequence, Organic device research today is conducted by actually fabricating the device and experimenting with them. Then, researchers theorize about the collected results. Although that methodology provides the most credible results, it may also lead to some confusion. Therefore, many combinations of parameters need to be materialized like material types and characteristics, doping, dimensions, fabrication conditions and processes. This is not only a time and personnel consuming task, but can also be expensive to carry out. The number of experiments, needed to answer questions, is also very large, due to the fact that experts are not allowed to focus on a certain issue. Instead, they need to consider and develop the design and the complete fabrication process of the device under study. In this thesis, a new method for developing a realistic model of any type of OFET is presented [20].

2.6.2 SILVACO

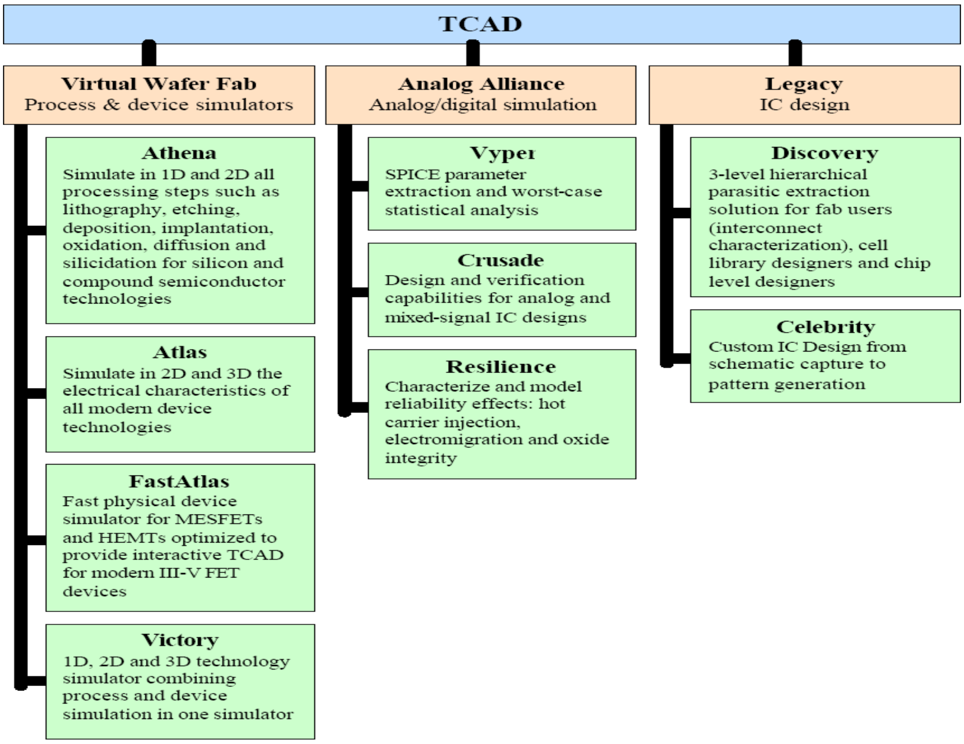


Fig 2.18: Silvaco's TCAD suite of tools

Silvaco is a company that specializes in the creation of simulation software targeting almost every aspect of modern electronic design. In their TCAD suite of tools, the company provides modeling and simulation capabilities for simple Spice–type circuits all the way to detailed VLSI fabrication.

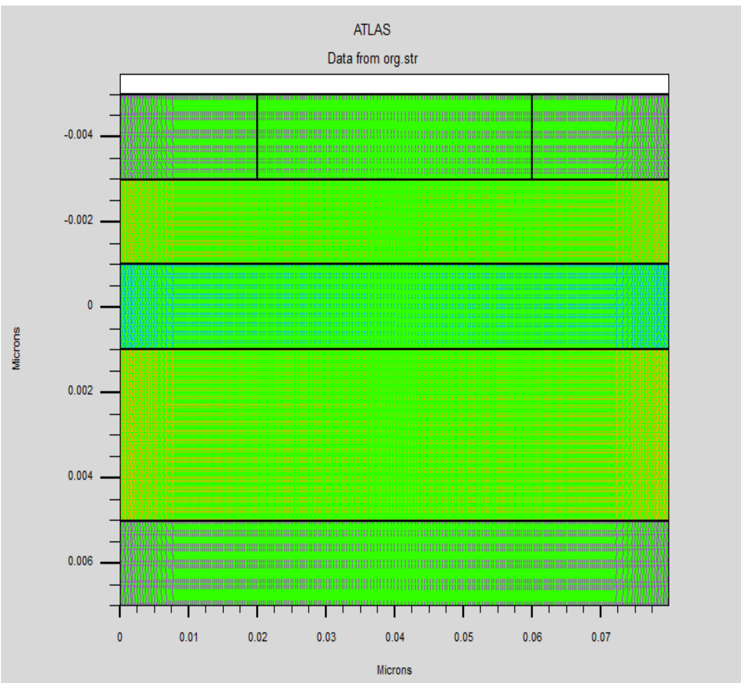
User–friendly environments are used to facilitate design and a vast number of different modelling options. The tools provide for creating complex models and 3D structural views. A wide variety of detailed layer-growth processes and material properties (e.g. mobilities, recombination parameters, ionization coefficients, optical parameters) add to the accuracy of the simulation. For this purpose, Atlas is a good combination of sophisticated in–depth device analysis in 2D or 3D. In addition, it abstracts away all fabrication details, shifting the focus of the modeler to the actual design. Like the rest of TCAD applications, it is based on hundreds of widely accepted publications, verified for their accuracy and correctness by numerous researchers [21].

2.6.3 Working with ATLAS-

Atlas can accept structure description files from Athena and Dev Edit, but also from its own command files. Since, for the purposes of this thesis, detailed process description is not required, the later is the more attractive choice. The development of the desired structure in Atlas is done using a declarative programming language.

MESH GENERATION

The first step the device is specifying the mesh in modeling on which the device will be constructed. This can be 2D or 3D and can be comprised of many different sections. Orthogonal and cylindrical coordinate systems are available. Mesh design is an important factor to design semiconductors in SILVACO ATLASTM. The data extraction points are used to sample electrical characteristics of the model at designated intervals. It is often used for accuracy and numerical efficiency that dictate the size of the sample intervals. Accuracy increases with finer grid points [22].




```
x.mesh loc=0.000    spac=0.0005
x.mesh loc=0.010    spac=0.00025
x.mesh loc=0.020    spac=0.00025
x.mesh loc=0.040    spac=0.00018
x.mesh loc=0.060    spac=0.00025
x.mesh loc=0.070    spac=0.00025
x.mesh loc=0.080    spac=0.0005

#
y.mesh loc=-0.005   spac=0.0005
y.mesh loc=-0.003   spac=0.00018
y.mesh loc=-0.001   spac=0.00025
y.mesh loc=0.001    spac=0.00018
y.mesh loc=0.005    spac=0.00025
y.mesh loc=0.007    spac=0.0005
```

Fig 2.19 - OFET Mesh Model

Material Specification

A library of materials is a part of the ATLAS tool. Many common materials can be selected from this library for use in defining material properties. Since solar cells are using state-of-the-art materials that may not be listed in the library, ATLAS has the ability to fully define new materials. A minimum set of property data must be specified for a new material to include band gap, dielectric constant, electron affinity, densities of conduction and valence states, mobilities, recombination coefficient, and an optical file containing refractive indices n and extinction coefficients k for a material [8]. The optical file determines the transmission and attenuation of light as it passes through the semiconductor.

user.material=P3HT

DOPING SPECIFICATION

Each region is allocated a type with a semiconductor material and level of doping concentration. Doping can either be n or p type with a choice of uniform, linear, or Gaussian distribution. The concentration units are the impurities per cubic centimeter.

Model Specification

General mobility model of organic material:

•Poole-Frenkel field-dependent mobility

$$\mu = \mu_0 \exp(-\frac{\Delta}{KT}) \exp(\gamma \sqrt{E}) \qquad \mathrm{cm^2V^{-1}S^{-1}}$$

$$\gamma = \mathrm{B}(\frac{1}{KT} - \frac{1}{KT_0}) \qquad \mathrm{V^{-1/2}cm^{1/2}}$$

Transport model (bulk)

• Space-Charge-Limited Current (SCLC): Poisson + Current continuity equations

• Hopping transport in disordered organic semiconductor

• Density of States

• Poole-Frenkel Mobility

Poisson Equation

$$div(\varepsilon \Delta \Psi) = -\rho$$

Current Continuity Equations $\frac{\delta_n}{\delta_t} = \frac{1}{q} div \vec{j}_n + G_n - R_n$

$$\frac{\delta_n}{\delta_t} = \frac{1}{q} div \vec{j}_n + G_n - R_n$$

$$\frac{\delta_p}{\delta_t} = -\frac{1}{q} div \vec{j}_p + G_p - R_p$$

• Drift Diffusion Equations $J_n = qn\mu_n \overrightarrow{E_n} + qD_n \nabla_n$

2.7 Fabrication OF OFET:-

Field-effect transistors are cleaned with ethanol and 2-propanol and then immersed in the in ethanol for different times. Before depositing the semiconductor layer, samples were taken out of the solution, rinsed with ethanol, toluene and 2-propanol, respectively, and dried with oven.

2.7.1 Solution-based deposition-

This technique can be used for polymer and small molecule OSCs, including spin-coating, dip coating and printing. This is a very efficient method to realize the organic film of high quality, large surface and low cost, especially the roll-to-roll printing, a promising way for the future organic electronics. Here we focus only on spin coating and deposition of organic semiconductor steps [23].

2.7.2 Spin-Coating:-

The spin coating technique is used to apply uniform thin films to the flat substrates. An excess amount of the solution is placed on the substrate, and then the substrate is rotated at high speed to spread the fluid by centrifugal force. Rotation is continued while the fluid spins off the edges of the substrate. The solvents are volatile, and simultaneously evaporate, so the higher the speed of spinning the thinner the film due to the layer centrifugal force. The thickness of the film also depends on the concentration of the solution and the solvent.

2.7.3 Vacuum evaporation-

This technique allows for deposition and purification of small molecule organic semiconductors. These materials are often used in OFETs in the form of thin film that could be grown by different processes: physical vapor deposition (PVD), chemical vapor deposition (CVD), pulsed laser deposition (PLD) and thermal evaporation technique [24].

Thermal Evaporation System:

a. Open air admittance valve and chamber. Load the sample. Pressure is now same as outside.
b. Turn on the Rotary Pump (RP). Vacuum the pipe and view in efficiency of RP in Perani gauge. It should be10^{-2}torr.
c. When perani gauge reading is 10^{-2}torr, then open the backing valve and air goes out.
d. Again close backing valve when Perani shows 10^{-2} torr and then roughing valve is on. Air in chamber goes out. Up to this total system is 10^{-2}torr as Diffusion pump (DP) cannot work unless chamber vacuum is 10^{-2}torr.
e. Now the roughing valve is closed and again backing valve is opened.
f. After opening the backing valve turn on chilled water (at4°C) and diffusion pump (DP).
g. Buffel valve is then opened. Limited number of air particle which were in the chamber goes out through DP and it can be seen in Perani gauge that maximum vacuum 10^{-6} torr (high vacuum) is reached.

h. Then power switch is turned on.

i. Metal melts and is deposited on the sample and after deposition buffel should be closed and DP should be turned off.

j. After 20 minutes of turning off of DP, chilled water circulation is made off backing valve is closed and finally RP is turned off.

k. Then by opening air admission pump air goes in and the sample is unloaded.

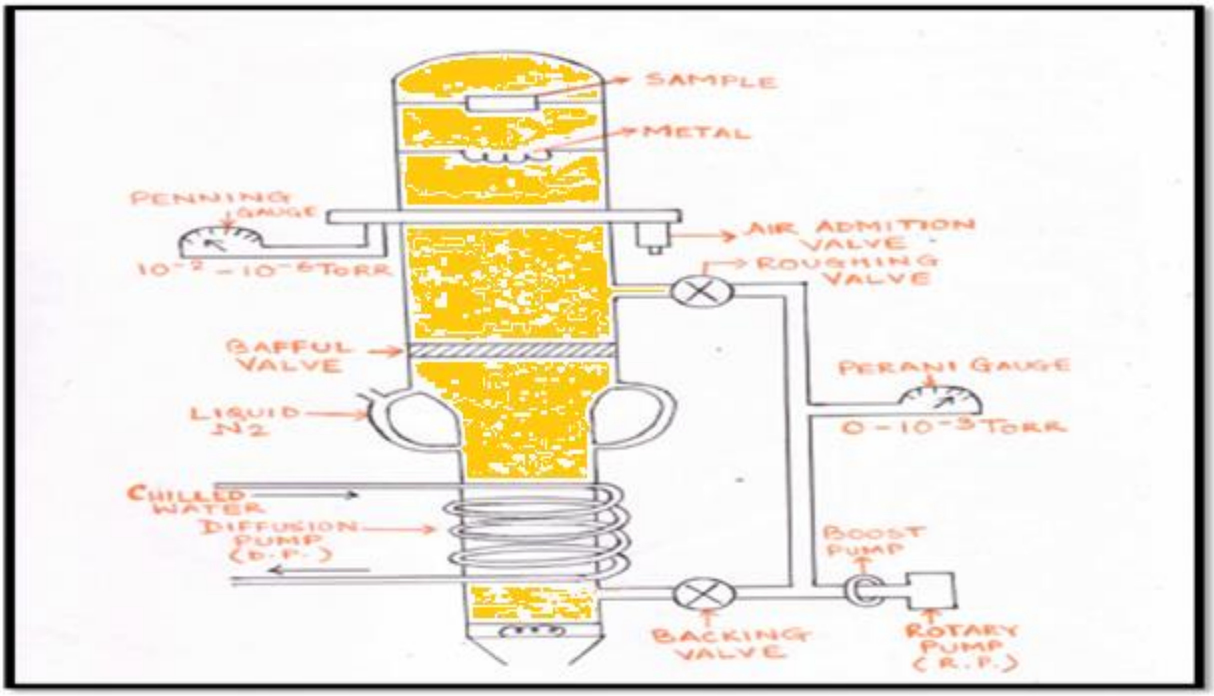


Fig: 2.20 General Vacuum Systems

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CHAPTER-3

PPV Based Bottom Gate Organic Field Effect Transistor (BGOFET)

3.1 Overview and Proposed Work:

In recent years there has been an increased demand for organic electronics. Organic field-effect-transistors (OFETs) are essential device capable for providing low-cost, flexible, lightweight, and environmentally-friendly semiconductors. OFETs deliver excellent key components for active matrix displays, radio frequency identification tags, and many other small scale integrated circuits. In fact organic electronics is an important topic in the area of display, sensor array, and photovoltaic etc. This will provide the chances of fabricating mechanically flexible devices on flexible substrates at low cost and low temperature. In 1962, the first Thin-Film Transistor (TFT) was reported by Weimer. Organic field effect transistors (OFETs) using organic semiconductors on inorganic dielectrics was reported after twenty years later. An organic field-effect transistor (OFET) is a Field-effect transistor (FET). We used an organic semiconductor in its channel. PPV based OFETs have been extensively tested and have exhibited highest mobility for hole transport. Field-effect transistors (FETs) using organic materials have generally low-speed due to their low-mobility, relatively high operation voltage. But in OFETS speed is not a limiting issue for many applications [1]. On the other hand there are many advantages to OFETs, such as the flexibility of the plastic fabrication substrate and the potential cost savings to manufacturers. One of the most widely studied organic semiconductor materials used for OFETs is PPV with 0.00001-0.0001cm^2/Vs carrier mobility. Therefore it is comparable value to hydrogenated amorphous silicon. OFETs on lightweight flexible substrates are expected to eventually replace hydrogenate amorphous silicon TFT applications on glass substrates. Here we used PPV poly (p- phenylenevinylene) as an active layer. Our proposed device will be used as a humidity sensor and different gas sensors in further optimization. The application of humidity sensors in agriculture, are plantation protection, soil moisture monitoring [2]-[6].

3.2 Device Structure And Parameters:

The 2-D cross-sectional view of the p-channel of our proposed device, Bottom Gate OFET (BGOFET) is illustrated in Figure: 1 in which organic polymer PPV acted as an active conducting layer i.e. channel region with L=80nm channel length.

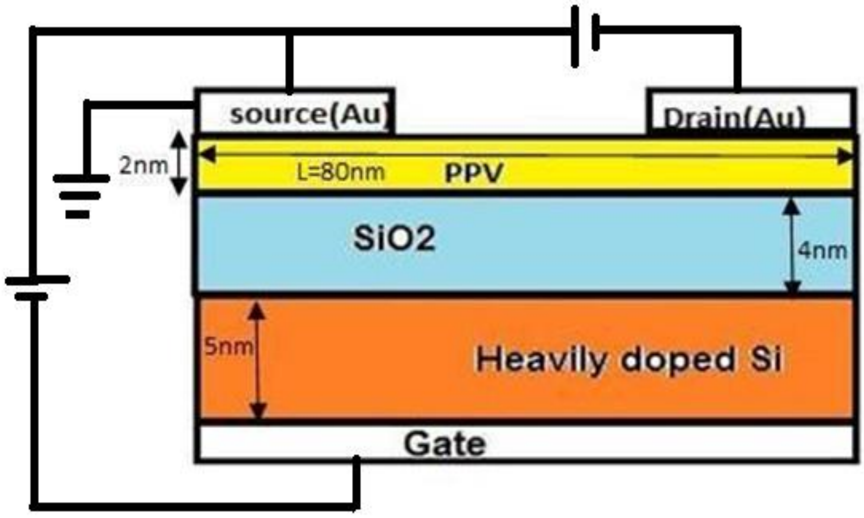


Figure 3.1: A cross-section of a PPV Organic Field Effect Transistor

Here organic semiconductor PPV is p-type doped with concentration $10^{20}cm^{-3}$ and thickness is 2nm. Metal (Au) is deposited on source, drain and gate region as electrode. Length of both source and drain region is 20nm and gate region length is same as channel length. The Doping specification of the OFET models are: P+ type source region ($1\times10^{20}cm^{-3}$) and same as the drain region, which are kept constant for all the simulations. Heavily doped silicon with n-type concentration $10^{16}cm^{-3}$ is placed between gate electrode and oxide layer, thickness of this silicon layer 5nm and oxide thickness is 4nm. The insulator can be made of a variety of dielectric materials, though SiO_2 (Silicon di-oxide) is a common choice. Table 3.1 summarizes all the parameters for the structure [7].

A voltage is applied to the gate metal to control the current flow from drain to source region. In our proposed OFET, due to the relatively high hole mobility p-type channel is used. A much higher negative voltage causes a p-type channel to form at the semiconductor-insulator interface. A drain to source negative voltage (V_{DS}) causing holes to flow from the source to drain and hence a negative current started from the drain to the source (I_{DS}). As the magnitude of the drain-source voltage (V_{DS}) is increased, $I_{DS}$is enhanced until “pinch-off," at which point the p-channel pinches closed on one side and the drain current saturates at its maximum value [8]-[11].

The ON/OFF current ratio is the ratio of the saturation current when V_{GS} is high at leakage current i.e. V_{GS} is zero. Better ratio provides better switching behavior of OFETs. In the inactive state, a low off current is desired to eliminate leakage. Our proposed device gives much satisfactory $I_{ON}/I_{OFF}$for our future applications. Here we proposed organic field effect transistor that enable to behave as sensor and give a result of Humidity Sensor and Gas Sensor.

Table 3.1 Device Parameters

Parameters	Dimensions
Source region length	20 nm
Drain region length	20 nm
Oxide thickness	4 nm (between channel and Si substrate)
Channel region length (L)	80 nm
Channel width	2 nm
Si substrate	80 X 5nm

3.3 Simulation Analysis:

We have used the 2D ATLAS TCAD software for the purpose of simulation. ATLAS predicts the electrical characteristics of the device by solving of coupled differential equations and drift diffusion model of charge transport using finite element method. The Poisson's equation and continuity equation for electrons and hole that are a set of coupled; partial differential equations are solved numerically with the help of ATLAS software [12-15].To obtain the terminal characteristics of the conventional devices, Lombardi mobility model (CVT), bandgap narrowing model, Fermi–Dirac statistics and the Shockley–Read–Hall and Drift-diffusion carrier transport models are used. It is considered that charge transport will become field dependent on inorganic materials at high electric fields ($\approx 10^5$V/cm).This phenomenon is described through a Poole-Frenkel mechanism. Field dependent mobility effects were also included within the simulations. The Poole-Frenkel field dependent mobility model is used in this simulation [16-19].

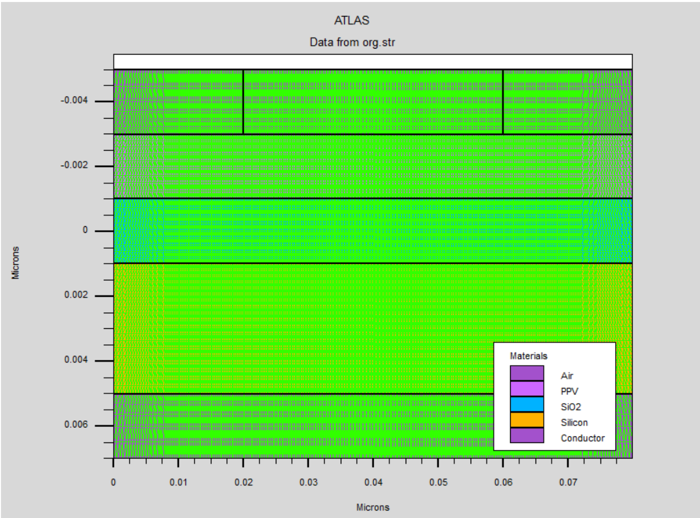
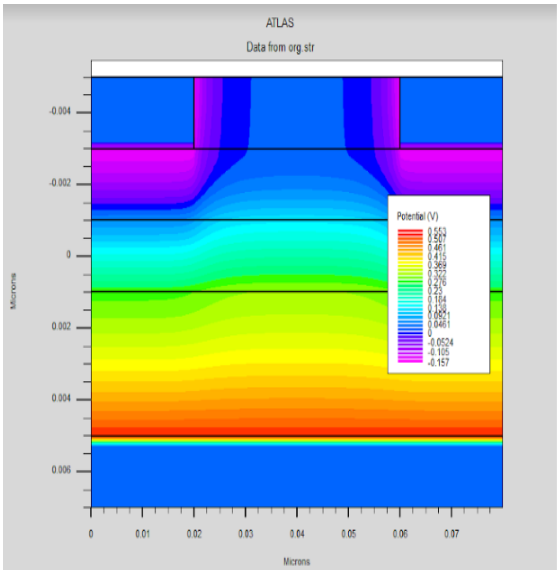


Figure: 3.2 Mesh analysis of simulated OFET structure

Here we can see in Figure 3.2 the mesh analysis of our proposed device in 2D SILVACO Atlas simulation. Mesh density near the interface of both source-channel (PPV region) and drain-channel is much higher, which give better electrical characteristics to this device.



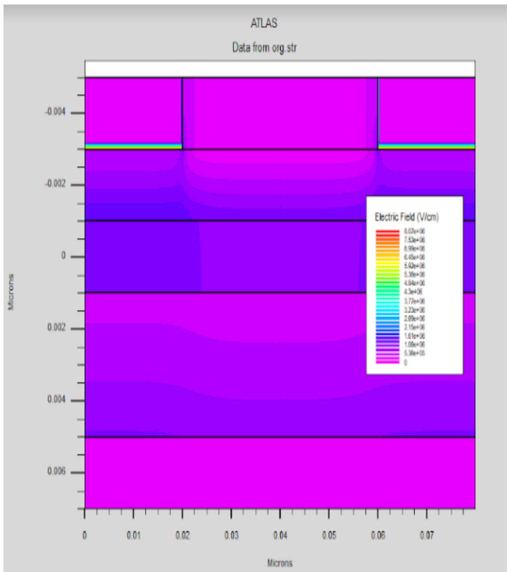


Fig: 3.3 Surface potential at the conducting layer and back gate potential. Fig: 3.4 Electric potential at the conducting layer and back gate.

The surface potential at the source end of the organic conducting layer adjacent to the PPV interface with the oxide layer and back gate potential at the end of the source close to the source electrode and drain end at the organic-oxide interface, back gate potential at the drain end which is close to the drain electrode are shown on the Figure 3.3. The potential at PPV-SiO2 interface at the organic conducting layer is varied with gate voltages.

Electric field is elaborated in the figure 3.4. Where the high electric potential is observed at the interface of both source- channel (PPV layer) and drain-channel (PPV layer).

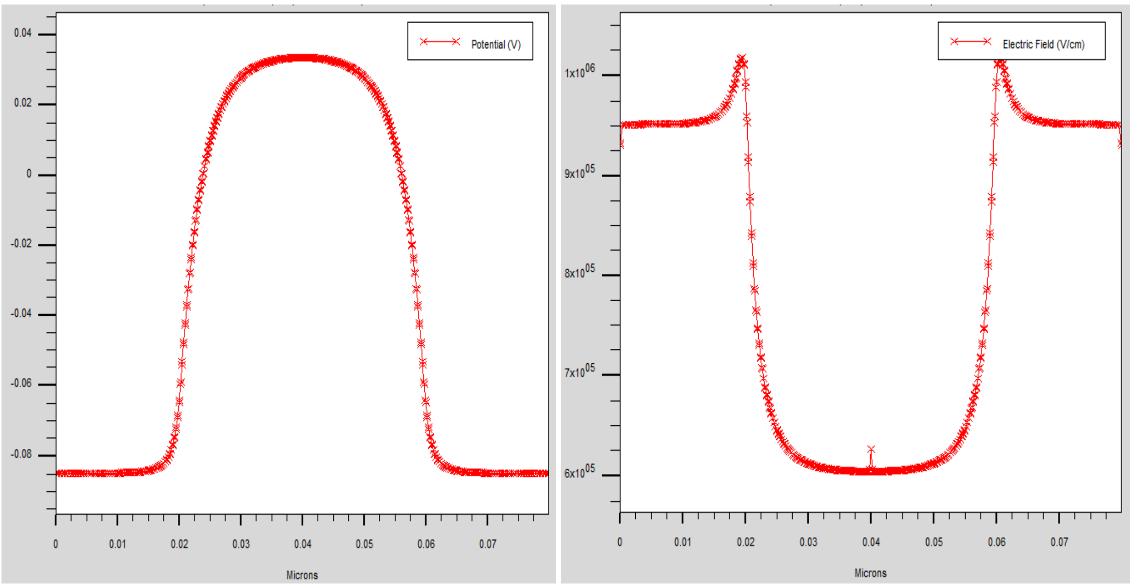


Fig: 3.5. (a) Simulated Surface Potential profile and (b) Electric field profile of BG-OFET.

3.4 RESULTS AND DISCUSSION:

3.4.1 Output characteristics:-

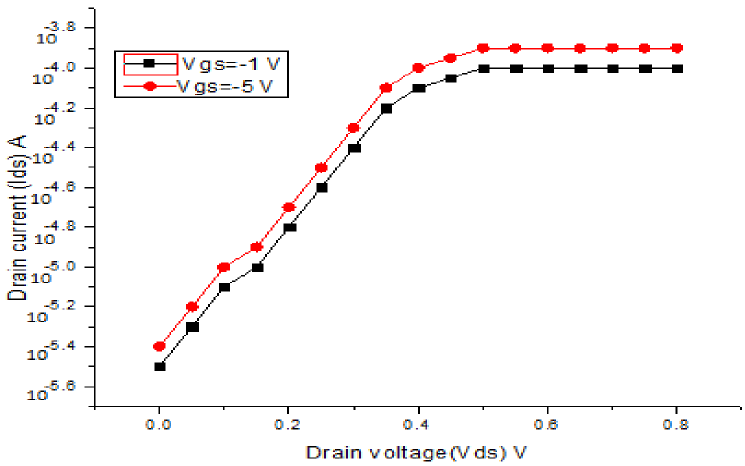


Fig 3.6: Output characteristics of BGOFET

Fig 3.6 shows Output characteristics of Bottom Gate Organic Field Effect Transistor at different gate voltages. Drain voltage Vds is swept to 0.2V and obtained characteristics for, -5V and -1V gate bias voltage. From the graph below, it can be observed that the Structure BG-OFET has highest ON current due to higher effective channel length and recorded very low OFF current, starting from 1×10^{-22}A, indicating minimum leakage compared to other conventional α-Si FETs. Therefore, the proposed structure has lower OFFT current and the structures have relative higher Ion/Ioff ratio other than standard OFET.

3.4.2Transfer characteristics

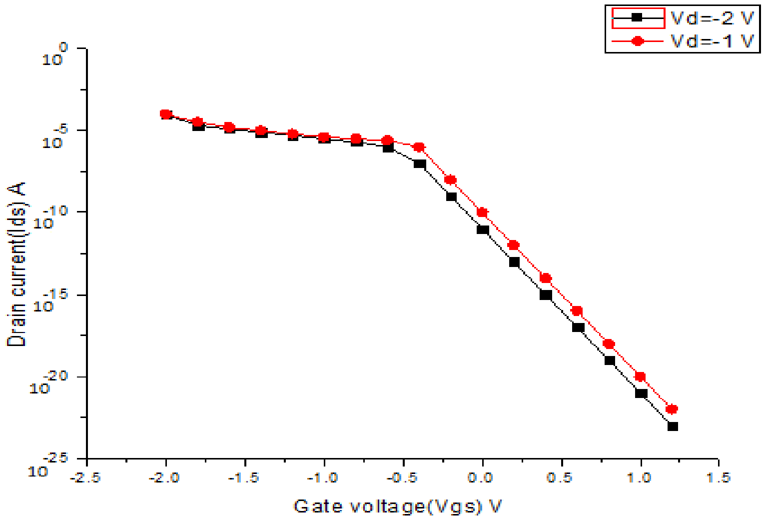


Fig 3.7 Transfer characteristics of BGOFET

From the graph we can observe the ON current is approx. 10-4 A which is much satisfactory. Performance parameters such as SS, Current ratio (ON/OFF) I_{ON}/I_{OFF} and Transconductance (gm) are extracted from resulted graph. Higher ON/OFF ratio provides effective switching behaviour.

Table 3.2: Extracted Parameters

Parameters	OFET
Subthreshold Swing (SS)	41mV/decade
ION/IOFF	10^{18}
Transconductance (gm)	2.2e-004

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CHAPTER-4

Simulation and Fabrication of Pentacene Based OFET

4.1 OVERVIEW AND PROPOSED WORK:-

Over the past few years there has been an increased demand for organic electronics. Organic field-effect-transistors (OFETs) are essential device capable for providing low-cost, flexible, lightweight, and environmentally-friendly semiconductors. OFETs delivered excellent key components for active matrix displays, radio frequency identification tags, and many other small scale integrated circuits. In fact organic electronics is an important topic in the area of display, sensor array, and photovoltaic etc. This will provide the chances of fabricating mechanically flexible devices on flexible substrates at low cost and low temperature. In 1962 the first Thin-Film Transistor (TFT) was reported by Weimer [1]. The first reports on organic field effect transistors (OFETs) using organic semiconductors on inorganic dielectrics appeared twenty years later. An organic field-effect transistor (OFET) is a Field-effect transistor where we used an organic semiconductor in its channel. Using organic materials Field-effect transistors (FETs) have generally low-speed due to their low-mobility, relatively high operation voltage. But in OFETS speed is not a limiting issue for many applications and it is possible to fabricate devices on flexible substrates with low cost. Among many organic materials, Pentacene is a p-type organic semiconductor material and the most prominent organic semiconductor material that has been widely used by other researcher in fabricating the organic devices. Pentacene based OFETs has a typical field effect mobility of around 10^{-5}cm2/V.sec [2].Therefore the carrier mobility of Pentacene devices is comparable with other α-Si devices. In 1991 the report of Pentacene mobility deposited using thermal evaporation was 0.002 cm^2/Vs by Horwitz et al. Later the mobility of the transistors using Pentacene was dramatically increased and reached the value of 1.5 cm^2/Vs during 1996-1997 [3].

In the past few years it is illustrated that the electrical performance of the Pentacene transistors is limited issue in carrier mobility, operating voltage and power consumption. A major factor is threshold voltage of the transistor. The device is operating in lower threshold voltage i.e. a lower turn-on voltage will be needed for the device. This Pentacene transistors voltage is same as the conventional transistors depends on the gate insulator thickness and its dielectric constant as well as the work-function of the gate electrode [4].

So to get the low power, the value of the threshold voltage should be low. The aspect ratio of the transistor is the ratio of the channel width to the channel length. The channel length is the distance between source and drain terminals. The channel width is the extension of the transistor. The field effect transistors can be divided into two groups depending on the type of the semiconducting channel to the p-channel and n-channel FETs. In the case of the n-channel FET the substrate is p-type and for the p-channel the substrate is n-type. The source and drain electrodes are n/n+ for the n-channel FETs and p/p+ in the case of the p-channel FET. The highly doped source-drain electrodes are chosen to have an efficient charge injection/collection from the electrodes and the channel. In the case of the p-channel field effect transistors, the gate-source and threshold voltages are negative. For the P-channel FET to turn on, the gate-source voltage should be smaller than the threshold voltage ($V_{gs}<V_t$) [5].Generally, the transistor is in the off state, when there is no current flowing through the channel and therefore the power dissipation of the device is zero. The threshold voltage of Pentacene transistors ranging is 2.67 V to -0.67 V. Therefore we can say that thickness reduction decreases the mobility and speed of operation.

In this paper, we propose a bottom gate OFET device composed of Pentacene as a conducting channel and SiO_2 as an insulator that has high ON/OFF current ratio and low ON voltage which will be used as a humidity sensor and different gas sensors in further optimization. The application of humidity sensors in agriculture, are plantation protection, soil moisture monitoring. The application of OFET transistor has such as electronic papers that are flexible and have been commercialized. Other applications such as RFIDs and sensors are still in the research communities and the market production will be beyond 2010. This device is compatible with low power applications. In this work, we only concentrate on simulation and fabrication of p-type OFET with top contact to evaluate and verify I-V characteristics [6]-[10].

In this thesis we fabricated a thin-film OFETs with pentacene on a SiO_2 gate dielectric followed by low-temperature aluminium deposition of the source-and-drain contacts. The FESEM (Field Emission Scanning Electron Microscopy) have been presented.

4.2 Device Structure And Operation:

The cross section of our proposed device, Bottom Gate OFET (BGOFET) is illustrated in Figure: 1 in which organic polymer Pentacene acted as an active conducting layer. In the bottom gate structure the electrodes can be deposited prior to or after the pentacene coating. This structure consists of a substrate, doped regions of semiconductors called source/drain, the source/drain with metallic contacts, insulator layer (silicon dioxide) and the gate electrode. The gate electrode can be either metallic or silicon/poly-silicon gate. Later organic semiconductor Pentacene is p-type doped with concentration $10^{17}/cm^3$and thickness is 2nm. Metal (Al) is deposited on source, drain and gate region as electrode. Length of both source and drain region is 20nm and gate region length is same as channel length. Heavily doped silicon with n-type concentration $10^{16}/cm^3$ is placed between gate electrode and oxide layer, thickness of this silicon layer 5nm and oxide thickness is 2nm. The insulator can be made of a variety of dielectric materials, though SiO_2 is a common choice. The source and drain electrodes is p/p+ in the case of the p-channel OFET [11].

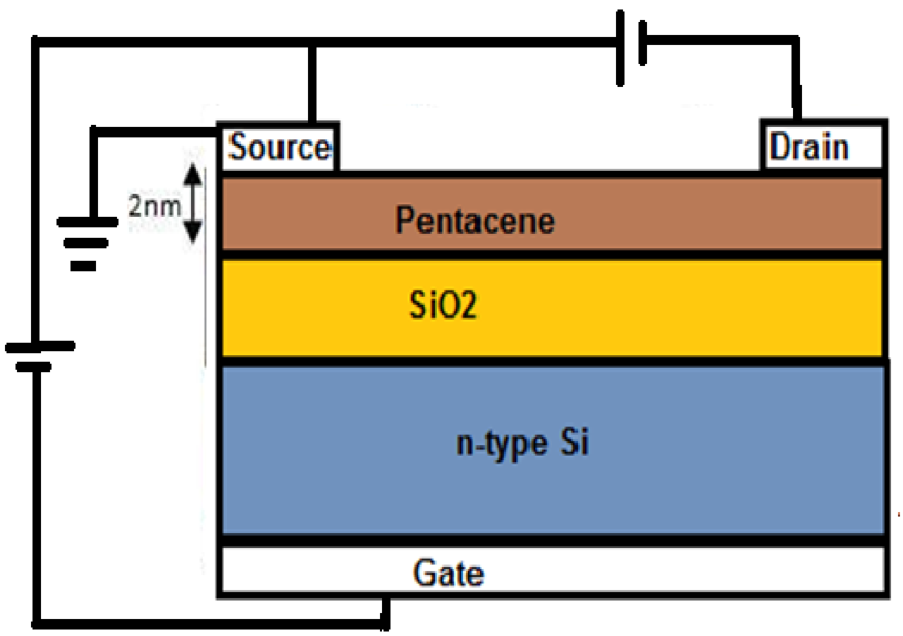

Figure 4.1: A cross-section of a Pentacene based Organic Field Effect Transistor

A voltage is applied to the gate metal to control the current flow from drain to source region. In our proposed OFET, the relatively high hole mobility p-type channel is used. A much higher negative voltage causes a p-type channel to form at the semiconductor-insulator interface. A drain to source negative voltage (V_{DS}) causing holes to flow from the source to the drain and hence a negative current started from the drain to the source (I_{DS}). As the magnitude of the drain-source voltage (V_{DS}) is increased, I_{DS} is enhanced until "pinch-off," at which point the p-channel pinches closed on one side and the drain current saturates at its maximum value. As the pentacene has p-channel transistor behavior, so the current equation derivation will be based on the p-channel FET. The current-voltage equation for the p-channel field effect transistor as: [11]-[15].

$$I_{Dlin} = -\frac{W}{L} C_i \mu \left[(V_{SG} - |V_T|).V_{SD} - \frac{V_{SD}^{\ 2}}{2} \right]$$

This equation is known as the equation for the p-channel transistor in the sub-linear region.

The saturation region equation is as:

$$I_{Dsat} = -\frac{W}{2L} C_i \mu (V_{SG} - |V_T|)^2 \quad , \qquad V_{SD} > V_{Sg} - |V_T|$$

The ON/OFF current ratio is the ratio of the saturation current when V_{GS} is high to the leakage current i.e. V_{GS} is zero. Better ratio provides better switching behaviour of OFETs. Our proposed device gives much satisfactory I_{ON}/I_{OFF} for our future applications. Here we proposed organic field effect transistor that enable to behave as sensor and give a result of Humidity Sensor and different types of Gas Sensor [16].

In this thesis the bottom gated configuration is used due to ease of fabrication. In the case of the bottom gated configuration the source and drain electrodes can be deposited before or after organic layer coating, leading to the bottom and top electrode configurations. In the bottom electrode configuration the electrodes are patterned and following that the organic layer is deposited. In case of top contact configuration the electrodes are deposited after organic layer coating. There are a few differences in performance. In the bottom contact configuration there is a thickness variation near the electrodes. In the top contact configuration there is a uniform contact between the electrodes and semiconductor. This results in a lower contact resistance and efficient charge injection.

4.3 SIMULATION RESULTS:

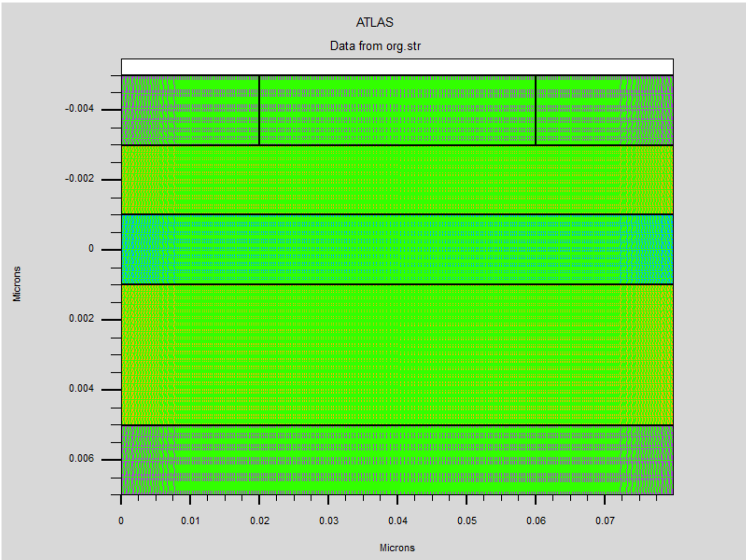

Figure 4.2: Mesh analysis of simulated OFET structure

Simulation was performed before experimentation in order to determine the I-V characteristics of the device. The 2D ATLAS TCAD software simulation software was used to study the electrical characteristics of the device by solving systems of coupled differential equations and drift diffusion model of charge transport using finite element method. An organic polymer Pentacene acted as an active conducting layer i.e. channel region with L=80nm channel length for simulation purpose we consider. Here organic semiconductor Pentacene is p-type doped with concentration 10^{17}cm-3 and thickness is 2nm. Metal (Al) is deposited on source, drain and gate region as electrode. Length of both source and drain region is 20nm. Heavily doped silicon with n-type concentration 10^{16} cm-3 is placed between gate electrode and oxide layer, thickness of this silicon layer 5nm and oxide thickness is 2nm [17].

Output characteristics of OFET:- Output characteristics of Organic Field Effect Transistor at different gate voltages and Transfer characteristics of OFET at different drain voltages are shown in Fig. 4.3(a) and (b), respectively.

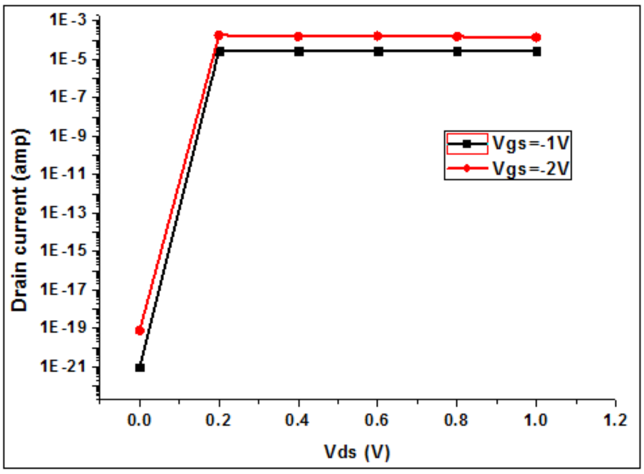

Fig 4.3(a): Output characteristics of OFET

Transfer characteristics of OFET: -

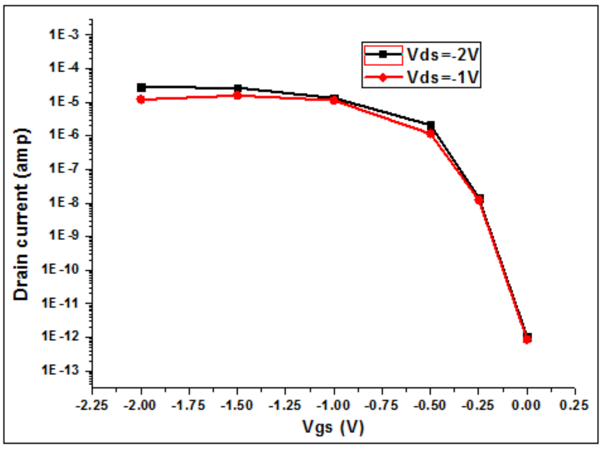

Fig 4.3 (b) Transfer characteristics of OFET

Figure 4.3 (a) shows the Output characteristics of Organic Field Effect Transistor i.e., typical drain-source current, I_{DS} characteristics of p-type OFETs with SiO_2 and Pentacene as dielectric and semiconductor layer at different gate voltages. The drain-source voltage, V_{DS} was varied 0 to -1.2 V in steps 0.2. Pentacene is a p-type semiconductor/active material, therefore the majority carriers are holes. We applied gate voltage; V_G was varied from -1V to -2 V state. The majority carries is holes for P-type OFET, therefore the holes channel is induced at the Pentacene and SiO_2 interface by a negative bias applied to the gate. The current flows form source to drain electrodes via holes channel if the $-V_G$ is sufficiently high. At this condition, the IDS are linear with $-V_{DS}$, which correspond to the linear region. As the –VDS increases, the space charge region under the channel and near the drain region widens and eventually reaches a pinch-off point condition in which the channel width becomes zero. Transfer characteristics of OFET at different drain voltages are shown in fig 4.3 (b), respectively. We applied drain voltage; V_{ds} was varied from -1V to -2 V state. From these curves, I_{on}/I_{off} ratio, the threshold voltage (V_{TH}) were 10^8, -0.7V respectively.

4.4 Experimental

Pentacene (P1802), (Mn=278.35 g/mol, purity >99%) was purchased from Sigma-Aldrich. The substrates used are commercially available. The thickness of silicon layer is 0.5 mm with resistivity 10^{-1} Ωcm; the thickness of the oxide layer on the Si is 0.5µm. It is highly Phosphorus-doped Si in (100) orientation. Pentacene derivatives are p-type semiconductors; having a highly doped and n^+ Si was used to gives more control on the conduction behavior.

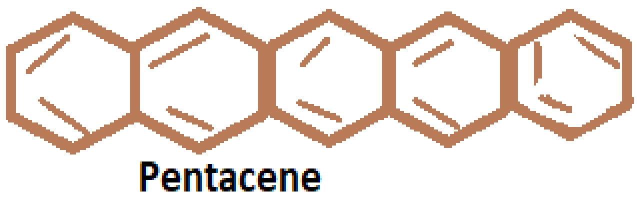

Fig4.4. - Structure of Pentacene

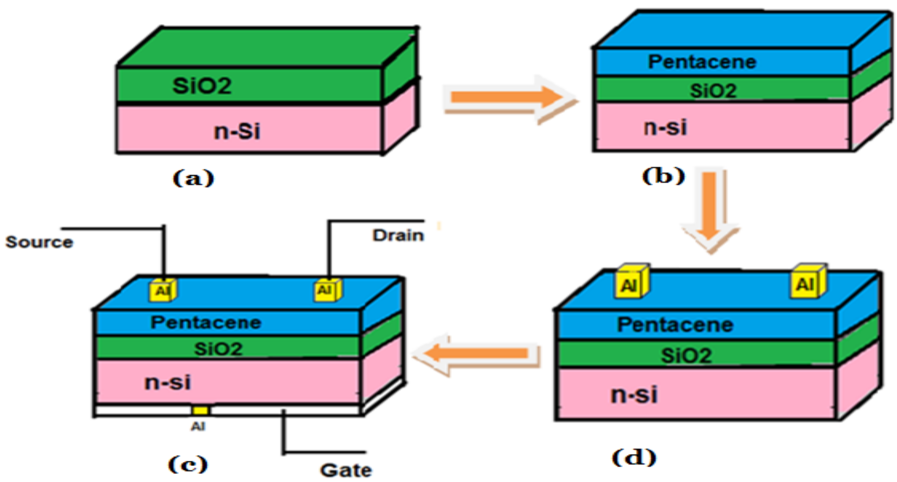

Fig4.5:-The fabrication steps of the OTFT (a) Oxidation of wafer. (b) Pentacene deposition using Synthesis Process. (c) Electrode formation of source and drain contact (e) evaporation of gate metal.

4.5 Device Fabrication

4.5.1 Oxidation of wafers

At first the substrate was cleaned with acetone for 10mins. At each cleaning step, the substrates were rinsed with de-ionized (DI) water for 5mins in an ultrasonic cleaner. To remove the acidic organic compounds, the wafers are cleaned using H2O:H2O2:NH4OH 5:1:1 at 70°C for 10 minutes and then pass it into cold water. To remove the organic compounds, the concentration of the sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) are used with 1:1 ratio followed by a rinse using deionized (DI) water. The next step is Alkaline Organic compound. The concentration of the H_2O, H_2O_2, and HCL are used with ratio of 6:1:1 and heat at 70^{0}C for 10 minutes and then clean in de- ionized water. The last step is the sample is dipped in 10% HF for 3 to 4 minutes. The cleaned substrates were rinse and dry in a vacuum oven for at least 30 min before use.This clean process takes approximately 30 minutes.

After the clean step the wafers should be loaded immediately in the quartz boat for the oxidation step. This insulator was grown on silicon wafer using wet oxidation and it took 30 minutes at 1000°C in a horizontal furnace. The furnace is programmed to have 10 minutes temperature ramp-up in nitrogen. In the case of the wet oxidation after temperature ramp-up the water valve of the furnace should be open and it took 1hours and then again dry oxidation for 30mins [18-20].

4.5.2 Pentacene Deposition using Synthesis Process

Before depositing the semiconductor layer, sample are cleaned with 2-propanol and then the sample were taken out of the solution and dry in a vacuum oven for 2 min. Pentacene solution was prepared using Solgel method. Pentacene solution was obtained by heating 100mg of Pentacene powder ($C_{22}H_{14}$) with 10mL Chloroform ($CHCl_{3)}$ at 60°C. Then, the mixture is stirred properly up to 1hrs and colour of the solution will be blue. Then Pentacene solutions were deposited on dielectric layer i.e. SiO_2 by using spin coating at 1500 rpm for 1 minute. The channel length is 200 μm [21].

4.5.3 Electrode formation:-After the pentacene deposition, source and drain electrodes were deposited by Al with thickness of 150 nm over the Pentacene layer using the thermal evaporation method under a pressure of 4x10^{-6} mbar. In the same way the gate electrode (Al) was thermally evaporated on Si wafer. Then, three copper wires are placed one by one inside the Ag paste and heated at 150°C for 15 min. The copper leads are taken for connection to perform the characteristic measurements of OTFT through the multimeter.

4.6 Results and Discussion

Fig. 4.6 shows the fabrication and simulation graphs obtained for transfer characteristics of OFET. Here we have considered drain voltage is -5V for simulation and fabrication of our structure. However, our proposed structure has an advantage of low threshold voltage than other conventional OFET structure. From this graph, we got two threshold voltages for fabrication and simulation -1.5V and -0.7V respectively for -2V gate voltage.

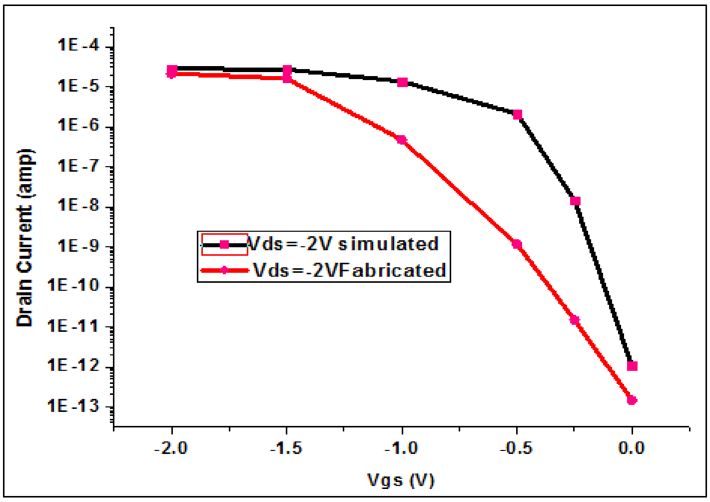

Fig. 4.6 Simulated and Fabricated I_D Vs V_{GS} profile of BG OFET

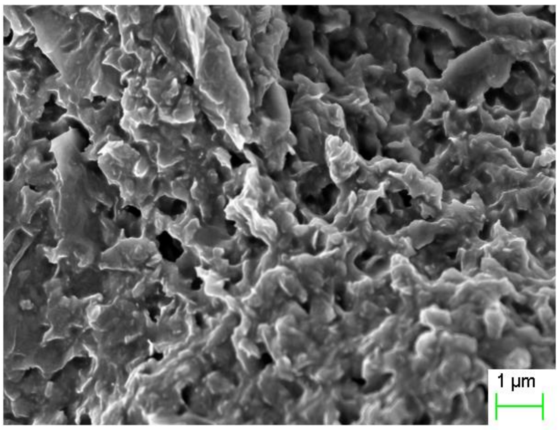

Fig 4.7-FESEM image of Pentacene based OFET sensor

Figure 4.7 is an FESEM image displaying the cross-section image of Pentacene/ SiO_2 thin film on silicon substrate at room temperature. The surface of the thin-film of Pentacene has grain sizes of few microns with an average size of 1 μm. FESEM image confirms that deposited thin film grown on the substrate is purely uniform and does not have any other scattered crystals on the thin layer of Pentacene.

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CHAPTER-5

PANI Based OFET Humidity Sensor

5.1 Overview and proposed work:-

Recent advancements in the field of sensor technologies have resulted in low power, miniaturized, high speed and cost effective sensor. Organic electronics is becoming an important research topic in the area of display, sensor array, and photovoltaic etc. OFETs delivered excellent key components for active matrix displays, radio frequency identification tags, and many other small scale integrated circuits .This will provide the chances of fabricating mechanically flexible devices on flexible substrates at low cost and low temperature. Conducting polymers (CPs) is mainly organic compound that contain π-orbital system through which electrons can move from one end to other of the polymer. Due to their mechanical flexibility, ease of processing and high electrical conductivity conducting polymer (CP) is attractive candidate for OFETs, organic photovoltaics (OPVs) and organic light-emitting diodes (OLEDs). CPs can be used to enhance speed, sensitivity and sort response time of sensors at room temperatur. There are several organic conducting polymer include Polyaniline (PANI), Polypyrrole (PPy), Poly(phenyl vinlene) (PPV), Poly(3,4-ethylene-dioxythiophene), PEDOT. Among these organic materials, PANI is a p-type organic semiconductor material with higher stability, high electrical conductivity and low processing cost and the most prominent organic semiconductor material that has been widely used by other researcher in fabricating the organic devices. Polyaniline (PANI) has been studied for many applications including logic circuit components, electromagnetic shielding, chemical sensing and anticorrosion due to its easy synthesis, room temperature operation, and relative environment stability. Sensors based on OFETs have several advantages, including high sensitivity, low cost, fast response, physical flexibility, and signal amplification via gate voltage [1]-[4].

Humidity sensors are useful for the detection of the relative humidity (RH) in various environments. PANI has been used in humidity sensor devices based on the electrical conductivity with water vapor. Polymers are the major class of materials for fabrication of humidity sensor. Humidity is a crucial ambient parameter which needs to be monitored for a wide range of applications such as instrumentation, automated systems, agriculture, and climatology. Organic polymer based material have been explored for the fabrication of humidity sensor. The application of humidity sensors in agriculture, are plantation protection, soil moisture monitoring. The sensing materials suitable for high performance humidity sensor must have high surface to volume ratio for better physisorption of water moleculs and the ability to interact with the water molecules repeatedly for enhance life cycle and faster response [5], [6].

In this paper, we propose a bottom gate OFET device composed of PANI as a conducting channel and SiO2 as an insulator which will be used as a humidity sensor. Using P-channel organic semiconductor i.e. Polyaniline as an active layer and gate insulator Silicon dioxide (SiO2) layer on n-type silicon substrate, humidity sensor based on organic field-effect transistor (OFET) was created. This device is compatible with low power applications. In this work, we only concentrate on fabrication of conducting polymer OFET with top contact to evaluate the humidity and verify I-V characteristics. The p-type OFETs operating in an enhancement mode with the current saturation (I_{Sat}) was 0.8μA and the threshold voltage V_T was found to be 2.2V.

The FESEM (Field Emission Scanning Electron Microscopy) have been presented. The results show that organic gate dielectrics possess potentially inexpensive alternative to inorganic counterparts and good electrical performance.

5.2 DEVICE STRUCTURE AND OPERATION:

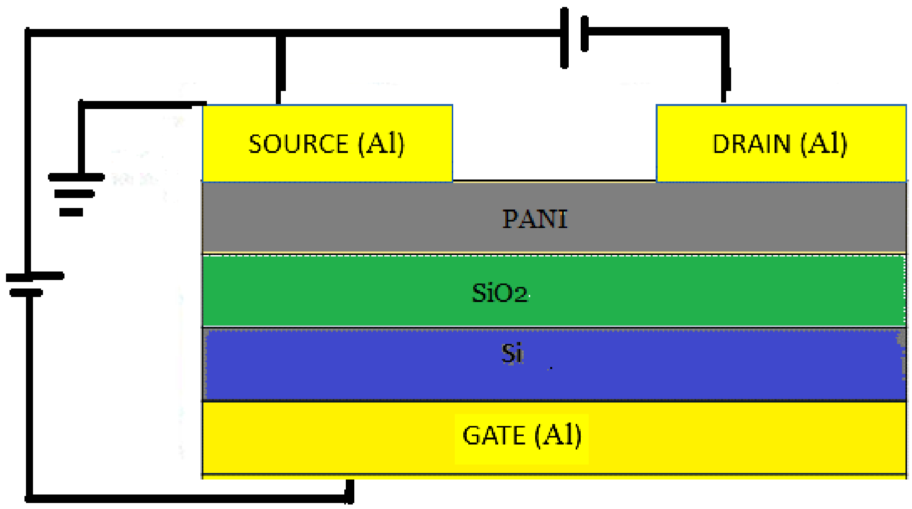

Figure 5.1: A cross-section of a PANI Organic Field Effect Transistor

The cross section of our proposed device, Bottom Gate OFET (BGOFET) is illustrated in Figure: 5.1 in which organic polymer PANI acted as an active conducting layer. In the bottom gate structure the electrodes can be deposited prior to or after the PANI coating. Here organic semiconductor PANI is p-type. Metal (Al) is deposited on source, drain and gate region as electrode [7]-[10]. N-type heavily doped silicon is placed between gate electrode and oxide layer, thickness of this silicon layer 0.5mm and oxide thickness is 2nm. The insulator can be made of a variety of dielectric materials, though SiO_2 is a common choice. A voltage is applied to the gate metal to control the amount of current flow from drain to source region. In our proposed OFET, the relatively high hole mobility p-type channel is used. A much higher negative voltage causes a p-type channel to form at the semiconductor-insulator interface. A drain to source negative voltage (V_{DS}) causing holes to flow from the source to the drain and hence a negative current started from the drain to the source (I_{DS}). As the magnitude of the drain-source voltage (V_{DS}) is increased, I_{DS} is enhanced until "pinch-off," at which point the p-channel pinches closed on one side and the drain current saturates at its maximum value [11]-[15].

5.3 Experimental Section-

5.3.1. Materials and Instruments:-

Polyaniline (PANI) was purchased from Sigma-Aldrich which was in liquid form (product number 650013). The properties of polyaniline in liquid form are enlisted below:

Form: Liquid

Concentration: 2-5 wt % in xylene

Particle size: <400 nm

Conductivity: 10-20 S/cm

Viscosity: ~3 CP (lit.)

Boiling point: 116°C

Density: 0.9-0.95 g/mL at 25°C

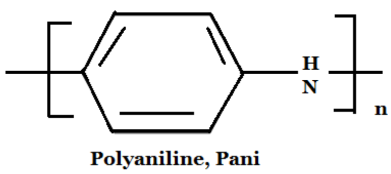

Fig 5. 2 - Structure of PANI

The substrates used are commercially available. The thickness of silicon layer is 0.5 mm with resistivity $10^{-1}\Omega cm$; the thickness of the oxide layer on the Si is 0.5 µm. It is highly Phosphorus-doped Si in (100) orientation.KEITHLEY 2635A system source was used to measure current-voltage characteristics of OFET. Scanning Electron Microscope (FESEM) was used.

5.3.2. Synthesis of polyaniline-

Polyaniline(PANI) solution was prepared using Solgel method. Polyaniline was dissolved in10ml N,N-Dimethylformamide (DMF). Then, the mixture is stirred properly up to 1hrs.The colour of the solution is green.

5.4 Fabrication of OFET-

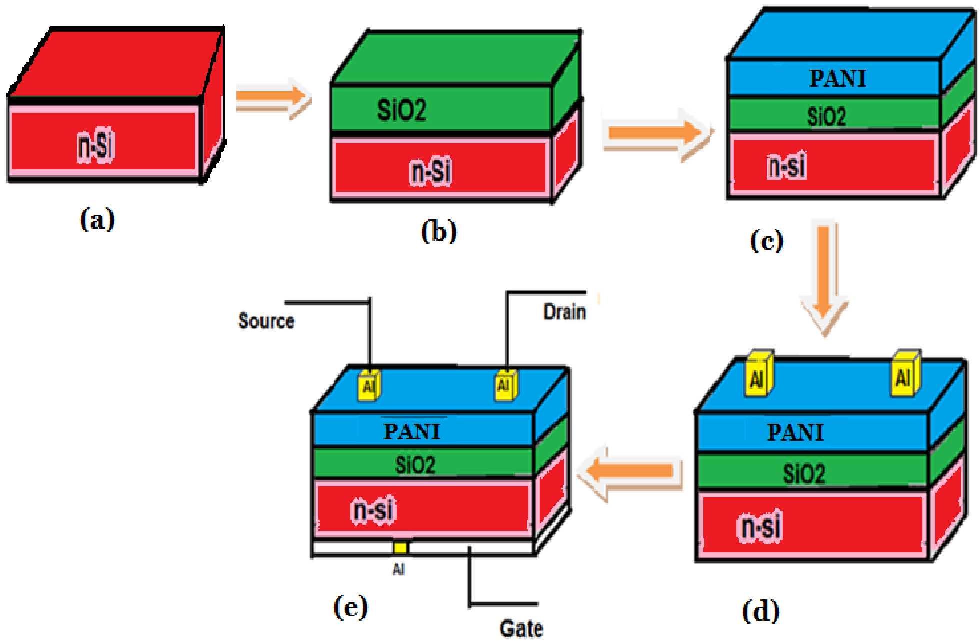

Fig- 5.3 Process flow used for fabrication of Polyaniline (PANI) based Field Effect Transistor. (a) Cleaning the n-type Si substrate. (b)Oxidation of wafer. (c) PANI deposition using Synthesis process. (d) Electrode formation of source and drain contact (e) evaporation of gate metal

5.4.1 Cleaning the Substrate-At first the substrate i.e. n-type Silicon wafer<100>was cut into small sample of dimensions 1.5 cm × 2 cm, and cleaned with acetone for 10mins. At each cleaning step, the substrates were rinsed with deionized (DI) water for 5mins in an ultrasonic cleaner. To remove the acidic organic compounds, the wafers are cleaned using $H_2O:H_2O_2:NH_4OH$ 5:1:1 at 76°C for 10 minutes and then pass it into cold water [16]-[18]. To remove the organic compounds, the concentration of the sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) are used with 1:1 ratio followed by a rinse using deionized (DI) water. The next step is Alkaline Organic compound. The concentration of the H_2O, H_2O_2, and HCL are used with ratio of 6:1:1 and heat at 70^0C for 10 minutes and then clean in de- ionized water. The last step is the sample is dipped in 10% HF for 3 to 4 minutes. The cleaned substrates were rinse and dry in a vacuum oven for at least 30 min before use.This clean process takes approximately 30 minutes.

5.4.2 Oxidation of wafers

Fig: 5.4 Diffusion Furnace.

After the clean step the wafers should be loaded immediately in the quartz boat for the oxidation step. This insulator was grown on silicon wafer using wet oxidation and it took 30 minutes at 1000°C in a horizontal furnace. The furnace is programmed to have 10 minutes temperature ramp-up in nitrogen. In the case of the wet oxidation after temperature ramp-up the water valve of the furnace should be open and it took 1hours and then again dry oxidation for 30mins [20].

5.4.3 Polyaniline Deposition using Synthesis Process

Before depositing the semiconductor layer, sample are cleaned with 2-propanol and then the sample were taken out of the solution and dry in a vacuum oven for 2 min. Spin coating method was used for conducting polymer film deposition. Then PANI solutions were deposited on dielectric layer i.e. SiO_2 by using spin coating at 4000 rpm for40 sec. The channel length is 100 µm and channel width is 2 mm.

Fig- 5.5 (a) PANI Synthesis (b)Spin coating

5.4.4 Electrode formation:-

After the PANI deposition, source and drain electrodes were deposited by Al with thickness of 150 nm over the PANI layer using the thermal evaporation method under a pressure of 4×10^{-6} mbar. In the same way the gate electrode (Al) was thermally evaporated on Si wafer. Then, three copper wires are placed one by one inside the Ag paste and heated at $150^{0}C$ for 15 min. The copper leads are taken for connection to perform the characteristic measurements of OTFT through the multimeter. The current-voltage characteristic of the OFET device was measured at different gate voltages (Vg) applied with DC power supply between source and gate, and the voltage was measured. I-V curves were measured at different humidity levels range of 65% RH.

Fig5.6 - Vacuum System

5.5 Results and Discussion

Figure 5.7 shows the characteristic curves of the drain current Id as a function of drain voltage V_d of p-channel OFET at various gate bias Vg under atmospheric environment with n-type Si gate, SiO2 gate insulator layer. The I_d of the active channel increases with increasing of negative gate voltage (Vg). The current saturation (I_{Sat}) is 0.8μA and the threshold voltage V_T is found to be 2.2V at Vg=-1V.

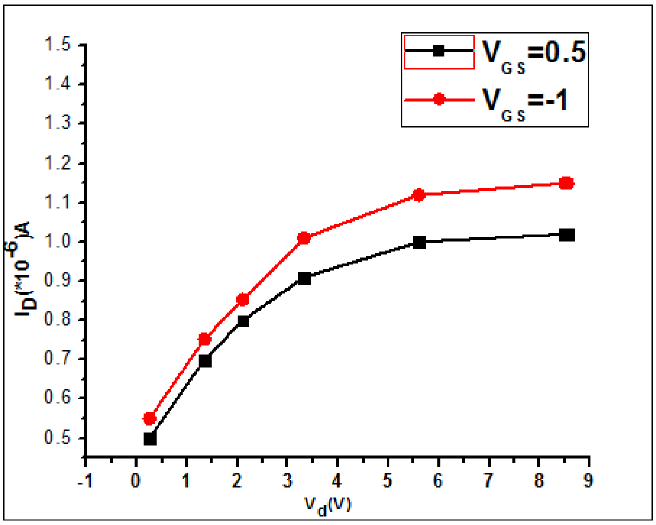

Fig. 5.7: Id vs. V_d as a function of Vg for OFET sensor.

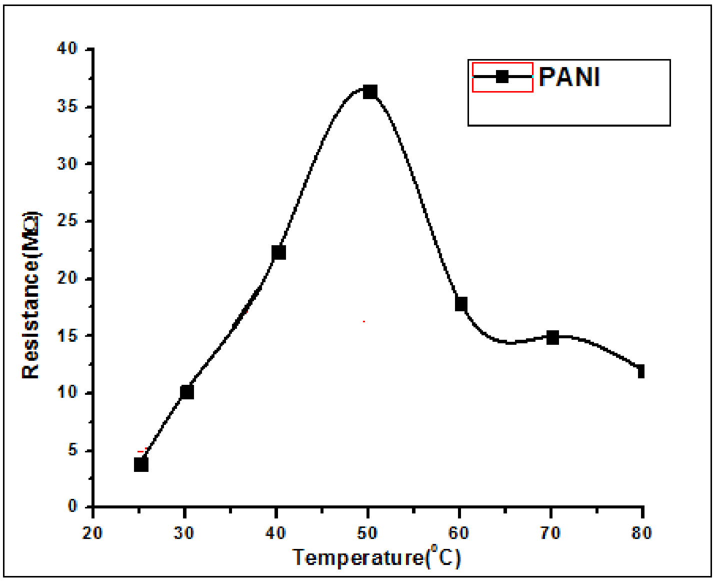

Fig 5.8-Resistance vs temperature graph

Figure 5.8 shows that the resistance of PANI decreases with the increase of the temperature. The decrease in the resistance or increase in the conductivity with the increase of humidity can be attributed to the mobility of the dopant ion which is loosely attached to the polymer chain by weak van Waals forces of attraction.

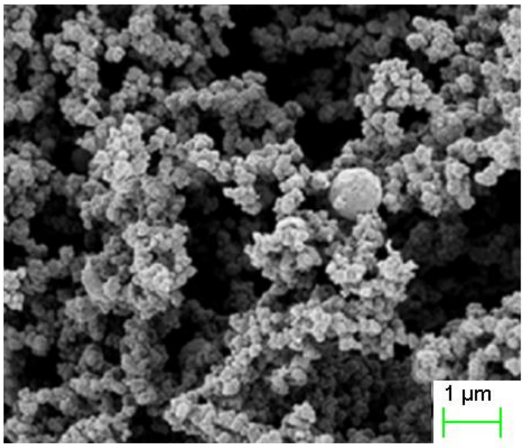

Fig 5.9-FESEM image of PANI based OFET sensor

Figure 5.9 is an FESEM image displaying the cross-section image of PANI/ SiO_2 thin film on silicon substrate at room temperature. The surface of the thin-film of PANI has grain sizes of few nanometres with an average scale size of 1 µm. FESEM image confirms that deposited thin film grown on the substrate is purely uniform and does not have any other scattered crystals on the thin layer of PANI.

The equation of relative response of the sensor (R):

$$R = [(Ra - Rv) / Ra] \times 100$$

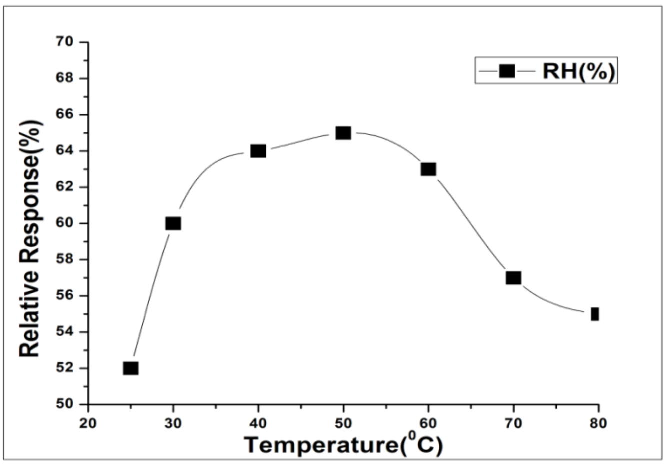

Fig- 5.10 Relative humidity vs temperature

It is observed that the PANI based OFET shows higher response at higher RH% obtained for p-channel. Due to rapid increase of mobile carrier value with respect to resistance value in presence humidity, the response of OFET of PANI is increase. Relative humidity increased from 63% to 65%. At higher values of relative humidity temperature decreased. However, relative humidity is inversely proportional to temperature as air warms it can hold more moisture so that the percentage of potential humidity decreases.

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CHAPTER-6

Application of TiO2-based thin film Capacitive Biosensor towards Fruit Freshness detection

6.1 Introduction-

Over the past few decades, existing techniques performing chemical experiments and have some drawbacks due to human fatigue, is expensive and time consuming. The demand for food industry owing to storage and preservation of food, it has to be developing methods that can easily track and preserve food freshness. Thus development of biosensors is selectivity, sensitivity, and stability, real-time and low cost techniques are used to overcome this problems [1].Nowadays there has been an increased demand for good quality, additive-free, nutritious and minimally processed food products. Health conscious consumers seek freshly-squeezed fruit juice that is sold under the label of 100% fresh fruit. These fruit juices are wholly made up of fresh fruits. After the fruits are harvested, natural metabolic activities and cellular respiration, causes change in the fruit quality such as firmness, pH, etc. Fruit freshness may be manually determined by the morphological characteristics (firmness and color) [2]-[5]. However, in bulk processing applications, manual determination of fruit freshness may not be feasible. Several sensory and instrumental techniques have been developed for the analyzing the quality of fruits. High-end instruments have been used extensively to study the composition and morphology of fruits. There are several existing methods to study fruit freshness based on studying the changes in chemical composition of samples. These include high performance liquid chromatography, gas chromatography with mass spectroscopy, etc. The traditional methods used to determine the shelf life of fruits and vegetables use chemical, physical and microbiological metrics such as bacterial counts, phenolic compounds, color and texture for sensory evaluation. These aforesaid methods are time-consuming and require highly-skilled personnel to operate the equipments and interpret the results. To study the morphology of fruits several image processing techniques have been used. In recent few years there has been an increased demand for high-speed, highly sensitive, cost effective and accurate sensors for the analysis and detection of chemical and biological analytes. Biosensors are essentially receptor transducer devices capable of providing selective quantitative or semi-quantitative analytical information using a biological or physical recognition element [6]-[8]. Biosensor consists of two components, a biological element which usually an enzyme detects the biological element, a transducer i.e. an electrode which converts the biological event into an electrical signal. A biosensor must be capable of providing rapid, real-time and reliable information regarding the biomolecule under study. Biosensors are also used in clinical diagnostics, environment monitoring, drug detection and food analysis [9].

Biosensor is categorized into three sections. (i) Sensor (ii) Transducer (iii) last section is the electronics, which comprises of signal conditioning circuit (amplifier), processor and a display unit [10]-[12].

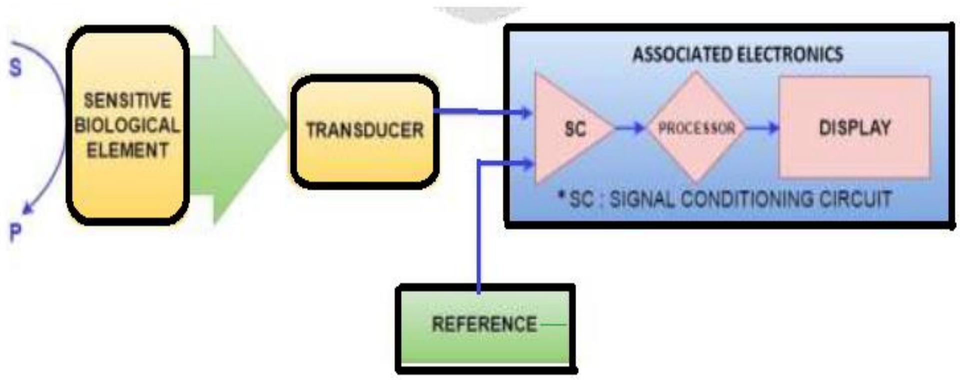

Fig -6.1: Schematic diagram of components of a biosensor

In this paper we have proposed a thin film based capacitive biosensor for the determination of fruit freshness. The sensor uses capacitance as a sensing metric and provides a cost-effective, low power and high speed means for the determination of fruit freshness without the involvement of bulky equipment or expensive image processing systems. Capacitive biosensors fall under the category of impedance biosensors. Biosensors are devices that use sensitive materials or structures to recognize the presence of certain materials and provide information regarding those materials. The detection of bio-molecules by electronic means using various micro and nanostructures has attracted a great deal of attention over the past few decades. In this work, a highly sensitive, robust and cost-effective capacitive biosensor has been proposed and its applicability towards testing fruit freshness has been experimentally demonstrated. The fabricated TiO_2-based thin film sensors are incorporated with microgap cavities which when embedded into the fruit surface becomes sensitive to any dielectric (Єk) changes that occur in the fruit during the phase of rotting. The sensors are hence based on the principle of dielectric modulation (DM) [13]-[18].

6.3 Proposed Sensor Model:-

The proposed model uses a fixed-plate capacitive sensor. In such sensors the capacitive coupling changes as a result of different materials placed near the plate. Capacitive sensors offer several advantages such as low cost, good stability and low power consumption. The model comprises of a multilayer structure. The capacitive plates are composed of silver. The silicon dioxide (SiO_2) layer acts as stable dielectric material. The stability of a good capacitive sensor is determined by the insulating properties of the formed recognition film. The insulated film is capable of eliminating unwanted redox reactions and can reduce the background current. Hence, SiO_2 is has been selected as the dielectric material. A layer of titanium dioxide (TiO_2) is sandwiched between the SiO_2 layers. Titanium dioxide is an n-type wide band gap semiconductor that is chemically stable, inexpensive and environment-friendly. Different metal oxide based thin film sensors have been fabricated for different sensing applications. WO_3 and TiO_2 are widely used in sensing applications owing to high stability, high sensitivity and non-toxicity. TiO_2 exhibits unique features of reversible change in conductivity, high sensitivity and biocompatibility, rendering it suitable for bio- sensing applications. The microgap cavities are formed by removing a fixed length of the SiO_2 layer.

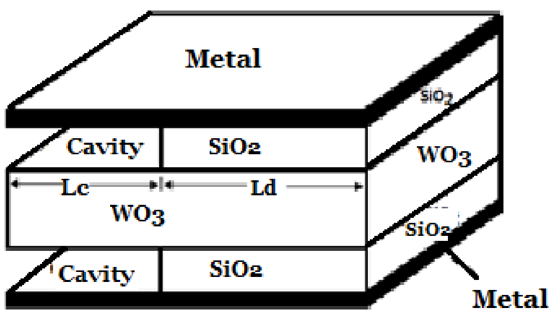

Fig 6.2: Capacitive biosensor model

The length of the cavity is denoted by Lc while the length of the SiO_2 layer is denoted by L_d. Fruits has unique values of dielectric constants owing to their different compositions. When the microgap of the proposed sensor is embedded into the fruit surface, the fruit pulp fills up the cavity. Changes in dielecric constant during the rotting phase of the fruit sample can be observed as change in capacitance value across the metal plates.

The biomolecules accumulate at the site of the microgap cavity. In the presence of the target biomolecules a change in the overall dielectric property of the silicon dioxide layer is observed. As a result, a variation in capacitance is observed across the plates of the capacitive biosensor structure. The capacitive sensor is based on the theory of electrical double layer. The electrical capacitance for a parallel plate capacitor is expressed as:

$$C = \frac{\varepsilon \varepsilon_0 A}{d} \qquad (1)$$

Where, ϵ_o is the permittivity of free space (8.85×10^{-12} F/m), ϵ is the dielectric constant of the medium between the plates, A is the surface area of the plates (m^2) and d is the thickness of the insulating layer.

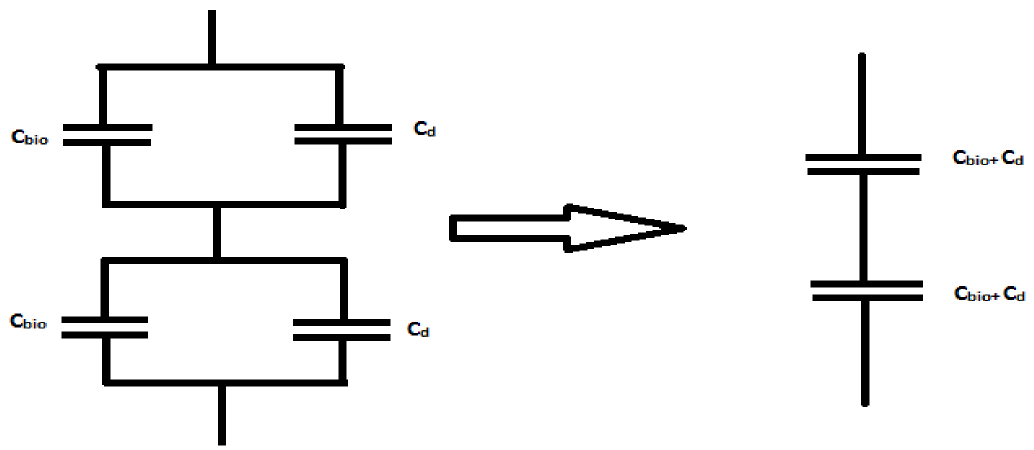

Fig 6.3: Equivalent capacitance of the sensor structure

Fig. 6.3 shows the equivalent capacitance of the proposed sensor. The capacitance across the cavity is expressed as C_{bio} while that across the silicon dioxide is expressed as C_d. The equivalent capacitance of the capacitive sensor system is expressed as,

$$\frac{1}{C_T} = \frac{1}{C_{bio} + C_d} + \frac{1}{C_{bio} + C_d} \qquad (2)$$

$$\frac{1}{C_T} = \frac{2}{C_{bio} + C_d} \qquad (3)$$

$$\therefore C_T \propto C_{bio} \propto \varepsilon_{cavity} \qquad (4)$$

Eq. (4) shows that the total capacitance, C_T is directly proportional to the capacitance of the cavity C_{bio}, which in turn is directly proportional to the dielectric constant of the cavity, ε_{cavity}.

6.4 Experimental Details

6.4.1 Materials And Methods

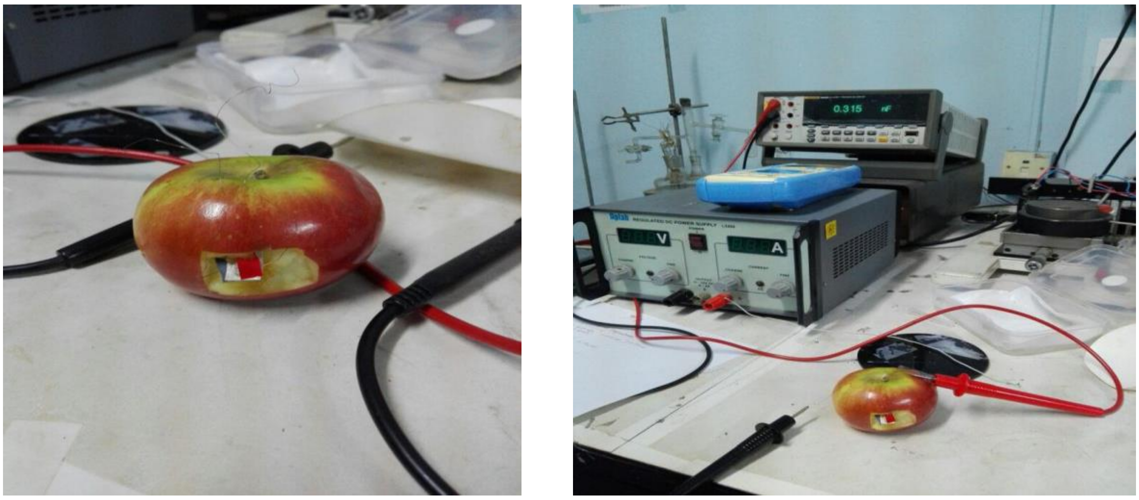

Fig 6.4: Experimental set up cavity based capacitive biosensors

Titanium butoxide was purchased from Sigma-Aldrich. The thickness of silicon layer is 0.5 mm with resistivity 10-1Ωcm; the thickness of the oxide layer on the Si is 0.5μm. A single specimen each of apple, orange and guava were tested for a period of 10 days with an interval of 24 hours between each reading. The capacitance across the biosensor was measured using a digital multimeter. The figure below shows the measurement setup for the capacitive biosensor for testing fruit freshness.

6.5 Fabrication of Biosensor:-

The p-type silicon wafer with 0.5 mm thickness was cleaned by acid cleaning process. Two wafer samples A and B were separately sent for oxidation to obtain the silicon dioxide layers. On the opposite side of the wafer, silver metal was deposited by metallization.

Preparation of thin film structure –

Sol–gel process is used to deposit the TiO_2 thin film on the silicon substrate (P-Si, resistivity 2–5 Ω cm and dimension 5 mm × 5 mm) because sol–gel is simple and low cost technique for deposition. TiO_2 was deposited by sol-gel method on sample A over the SiO_2 layer. 2 gm of titanium butoxide was mixed with 20 ml of ethanol and vigorously stirred for 20 mins using magnetic stirrer. Then 0.2 CC HCl was added drop wise while stirring. The transparent solution was kept for two days. Milky white TiO_2 was obtained which was dip coated onto the sample A. Sample A and B were sandwiched together with silicon dioxide layers facing each other. PDMS was used to improve adherence. The formation of an ultrathin polymer layer on the electrode leads to increased diffusion sensitivity. The sensor is coated with tape on three sides and etched on one side using HF. The silicon dioxide is partly etched in presence of HF creating the sensing cavities [19].

Electrode formation:-

Metal contacts are made on the capacitive plates using silver paste to facilitate measurement. On the opposite side of the wafer, silver metal was deposited by metallization.

6.5 Results And Discussion

Fig. 6.5 shows the variation of capacitance with number of days for apple, orange and guava fruit samples. The observed capacitance is in the range of nano farads (nF). It is seen that as the fruits begin to rot, i.e, over the observation period of 10 days, the capacitance value for all three fruit samples decreases. This can be used as a sensing metric to determine the freshness of the fruit samples.

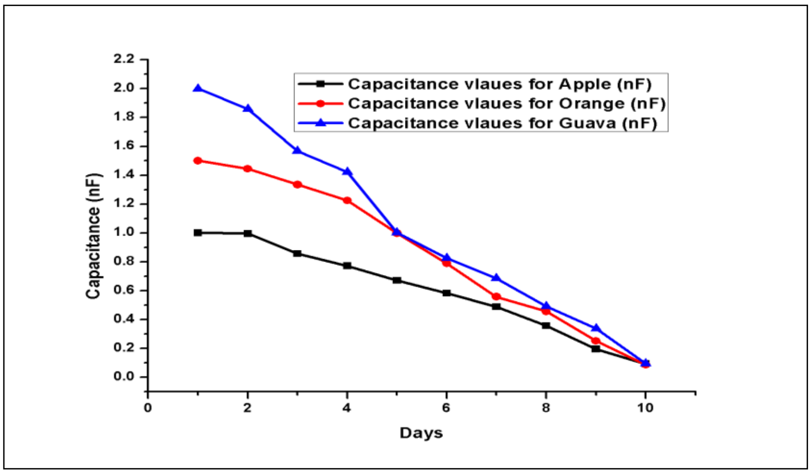

Fig 6.5: Capacitance versus No. Of days plot of three different fruits samples (Apple, Orange, Guava).

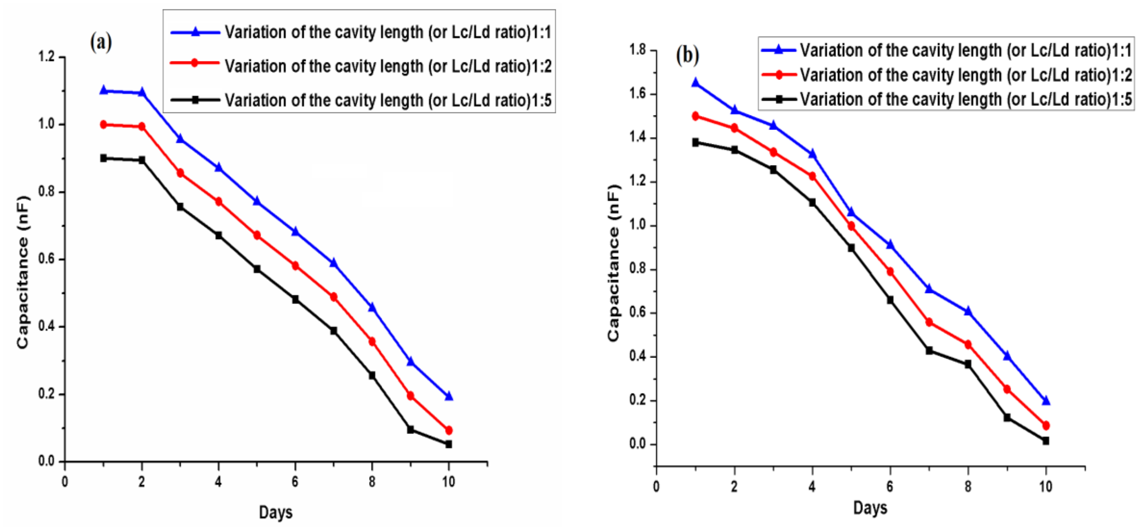

Fig 6.6: Results of Capacitance Vs Days with varying cavity length for (a) Apple (b) Orange.

Fig.6.6. shows the plot for variation of capacitance over the observation period for different cavity lengths (Lc). It is observed that as the cavity length is reduced, the capacitance value obtained is larger. However, there is no significant change in sensitivity as a result.

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Chapter-7 Concluding Remark and Future Aspects

7.1 Conclusion-

The objective of the work is to analyze the credibility of Devices like OFET; Biosensor based devices to function as future devices. The independent assessment on every device is differently analyzed for distinct applications. All three devices indicate better characterization than conventional α-Si FETs. In these thesis novel derivatives of Polymer based OFETS are characterized electrically. Therefore, it can be concluded that OFET is more suitable for applications in large area of electronics and different types of sensors. This outcome can be further explored and use in the field of low power, applications, low-cost, (RFID) tags, sensor devices, organic active matrix displays applications. And last one is Biosensor which is used to detect fruit freshness.

Chapter-2

In this chapter, at first we discussed organic semiconductors physics: small molecular, polymeric and n-type semiconductors; and some typical organic semiconductors and their applications. And, then OFETs structures (configurations) were discussed. And then, we deal with the principal parameters related to the performances of organic semiconductors: mobility threshold voltage, contact resistance, subthreshold slope etc. Due to comparable performance to conventional amorphous inorganic semiconductor materials, Organic semiconductors will become more attractive. Furthermore, it has some advantages of large-scale fabrication with low-cost, solution-based film deposition processes at low temperatures with high charge carrier mobility.

Chapter-3

In this proposed work, the simulation of PPV based OTFT is illustrated. In addition to having a higher mobility value, the on/off current ratio for PPV OFETs can reach 10^{18}, indicating its ability to function very well as a switch. This gives the good result in terms of low threshold voltage (V_T). It can be concluded that OTFT has shown better performance in terms of saturation current.

Chapter-4

In this proposed work, Pentacene-based OFETs with SiO2 insulators is illustrated. Moreover, the low-temperature-fabricated pentacene-based OFET with SiO2 insulator also shows good electrical properties. A excellent mobility value, the on/off current ratio for Pentacene OFETs can reach2.7 x 10^4, indicating its ability to function very well as a switch. This gives the good result in terms of low threshold voltage (V_T) i.e. -1.125V. The excellent interface properties and microstructures of pentacene films play an important role in the good electrical properties of pentacene-based OFET with SiO2 insulator. Through this work we have done the Fabrication of the OFET device and OFET based sensor and verification of the simulated results.

Chapter-5

OFET based on PANI/SiO2 composite film was fabricated. It is used as humidity sensor. The performance of this sensor was evaluated using current-voltage characteristics under exposure of different humidity. The Id of the PANI active channel is enhanced with the increase of negative gate voltage Vg. Also, the current saturation (I_{Sat}) was found to be 0.8μA and the threshold was found to be 2.2 V. The higher response of the sensor was obtained 65% from PANI p-channel. Therefore, it can be concluded that PPANI based OFET is more suitable for applications in large area of electronics and different types of sensors. This outcome can be further explored and use in the field of low power, applications like low-cost (RFID) tags, sensor devices, organic active matrix displays applications.

Chapter-6

Biosensor: In this work, a TiO2-based thin film capacitive biosensor has been fabricated with microgap cavities. Fruits have distinct values of dielectric constants which vary during the rotting phase of the fruit due to chemical changes. When the microgap cavity is brought in close proximity to the fruit pulp, diurnal changes in the dielectric constant is reflected as variation in capacitance across the metal plates of the sensor. The sensor was tested for fruit freshness detection on three fruit, namely, apple, orange and guava. It was observed over a period of ten days that as the fruit begins to rot, the capacitance values reduce. The proposed capacitive biosensor can be developed into a cost-effective and portable sensing system and has the potential to replace the bulky and expensive instruments that are presently used for the determination of fruit freshness.

7.2 Future Scope:

In case of OFET further improvement can be achieved with the use of novel structures to enhance the electrical characteristic such as increasing the carrier mobility or controlling the threshold voltage. This is compulsory for controllable operation of OFET transistors especially for the circuit applications. The type of the insulator layer is a crucial parameter that influences the electrical performance i.e High field-effect mobility, Low threshold voltage and subthreshold slope, High ON/OFF ratio and low OFF-current.

In case of Biosensor, reduction in physical size of the device and multi-array analysis are preferred without compromising the specificity and sensitivity of the device at the same time. Multifunctional biosensing systems are required using a single device for analysis of multiple analytes. Novel biosensing materials aimed at high sensitivity, selectivity, stable and low material synthesis cost will boost the market for biosensors and also their applications in different areas. The next generation of biosensors based on nanostructures could lead to a construction of devices able to markedly compete with other analytical methods used today. Applications of nanomaterials in biosensors provide opportunities for building up a new generation of biosensor technologies. Nanomaterials improve mechanical, electro- chemical, optical and magnetic properties of biosensors and are developing towards single molecule biosensors with high throughput biosensor arrays. Nanomaterial-based biosensors show great attractive prospects, which will be broadly applied in clinical diagnosis, food analysis, process control, and environmental monitoring in the near future.

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