Fabrication and characterization of CuPc and PCBM based organic solar Cell

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Certificate

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Dedication

I dedicate my effort to the builders of nation and my teachers.

Acknowledgment

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Abstract

Organic solar cells have potential as an alternative to conventional inorganic solar cell due to low processing cost, flexibility and easy fabrication technique.

The goal of this paper is to study the characteristics of the CuPc and PCBM based organic solar cell and traps identification by introducing a thin layer of Ag at the interface of donor (CuPc) and Acceptor (PCBM), their photovoltaic and optical properties were investigated. The heterojunction solar cells with silver inter layer and without silver were fabricated through thermal deposition in HR vacuum. The OPV solar cells were characterized using current-voltage graphs, absorbance spectrum and Impedance spectroscopy. Impedance spectroscopy was taken to identify these traps using series resistance, parallel resistance, and Impedance spectrums under different frequencies and optical behaviors of these devices have been investigated with absorbance spectrum.

Introducing Ag to interfacing point decreased Voc, Isc, FF, and efficiency due to generation of charge traps by Silver. And these traps were identified using IS, series and parallel resistance. The effect of donor/ acceptor and silver interlayer thicknesses was also studied.

Keywords. HR thermal evaporator, I-V characteristics, Impedance spectroscopy, Optical properties

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List of journal paper

1. Muhammad Ahsan Naveed, Dr. Parvez Akhtr, Dr. Afzal Hussain, Dr. K. Islam, "Fabrication and Characterization of CuPc and PCBM based organic Solar cell with metal Interlayer" Journal of International academic research for multidisciplinary (Paper accepted).

- Attached at Annexure I

List of abbreviation

OPV	Organic Photovoltaic
CuPc	Copper Phthalocyanines
PCBM	Phenyl C_{60} Butyric acid Methyl Ester
Ag	Silver
ITO	Indium tin oxide
Al	Aluminum
PV	Photovoltaic
D	Donor
A	Acceptor
PCE	Power conversion efficiency
UV	Ultra Violet
CIGS	Copper indium gallium selenide
DSC	Dye-sensitized sells
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
OSC	Organic solar cell
ISC	Inorganic solar cell
IQE	Internal quantum efficiencies
PL	Photoluminescence
Voc	Open circuit voltage
Isc	Short circuit current
FF	Fill Factor
EBL	Exciton Blocking Layer
AM	Air Mass
QE	Quantum Efficiency
CE	Conversion Efficiency
CVD	Chemical vapor deposition
PVD	Physical vapor deposition
HR	Heat Resistive
EB	Electron Beam

CSS	Close-Spaced Sublimation
CSVT	Close-spaced vapor transport
HCL	Hydrochloric acid
DI	De Ionized
IPA	Isopropanol acid
QCM	Quartz Crystal Monitor
UV-VIS-NIR	Ultraviolet Visible near Infrared
LCR	Inductance Capacitance Resistance
IS	Impedance Spectroscopy

Chapter 1

INTRODUCTION

1.1 Background

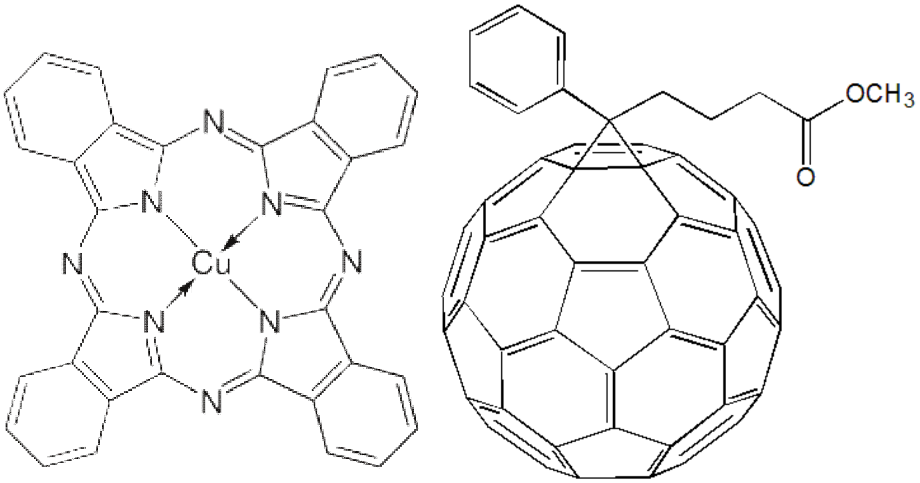
Organic Photovoltaic (OPV) solar cells are emerging as a third generation of photovoltaic technology. The OPV provides assurance of a low cost solar photovoltaic solution and attracts important academic and industry research. These OPV solar cells have number of benefits over inorganic solar cells. Organic materials are rich to form a solid base for material innovation; the OPV materials have much higher absorption coefficients than silicon, Low energy processing, non-toxic and environmental friendly. The OPV devices are under considerable examine more than previous 25 to 30 years [1, 2]. In spite of efforts, the performance of device is still far-off from the mandatory practical application. Limiting factor used for performance is primarily the small exciton diffusion length as match up to the optical absorption. That is why the width of active charge partition plus collection region is minute. This results in reduction in cell efficiency.

Different techniques have been used to overcome these issues like short diffusion length, width of active region etc. Including use of intercalated conjugated polymer blends [2], charge separation interface, use of high exciton diffusion length materials [3], with alternative geometries of cell e.g. a cell having mixed region of co-deposited pigments inserted among donor acceptor layer [4], and staked tandem solar cell [5]. In tandem solar sell two heterojunctions are deposited. These are separated by a metal layer. The technology has advanced in different device structures including donor/ acceptor heterojunction, tandem structures, and the use of electrically doped transparent layers. The efficiency of all devices could increase from improved understanding of the physics of exciton separation at the donor– acceptor interface.

In this work new approach is adopted in which donor (CuPc) and acceptor (PCBM) were deposited one by one and separated by a thin Ag metal layer. CuPc has high optical, light stability, chemical stability and photovoltaic property. Therefore CuPc was used as a donor material in organic solar cells [6]. It was found that metal layer takes charge from the donor acceptor interface and produced traps which recombine the electrons and hence reduced the Voc and Isc of the device. To identify these traps we perform Impedance spectroscopy, using series resistance (Rs), parallel resistance (Rp), and impedance spectrum with changing frequencies. Optical behavior of these devices was also observed to understand their optical properties.

Solar cells are the semiconductor devices that convert light (photon) in to electrons or electricity. Organic solar cells and inorganic solar cells accomplish this phenomenon differently.

1.2 Structure of Organic Materials



(a) (b)

Fig. 1.1 structure of CuPc & PCBM

Fig. 1 shows the structure of donor and acceptor materials. CuPc used as a donor material, it is an excellent electron donor material, Phthalocyanines have a photovoltaic property, heat-resistance, light-stability, and high optical absorption in the visible range, and are used in semiconducting devices and solar cells as a donor material.

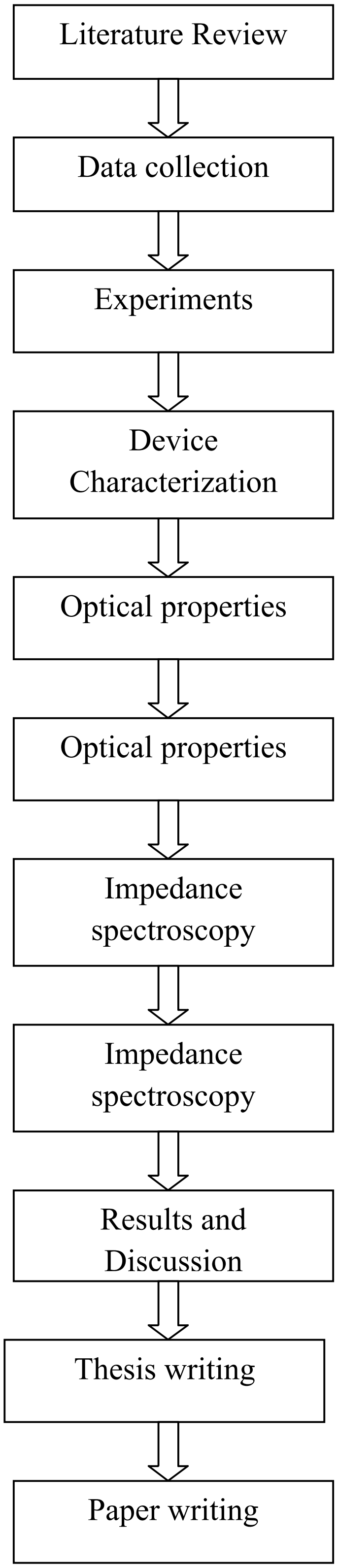
PCBM is used as acceptor material; it is excellent electron acceptor material as well as frequently used in solar cells and flexible electronics in combination by means of electron donor materials like P3HT and CuPc. It is a further practical option for electron acceptor as it compared with fullerenes.

1.3 Objectives of study

The objective of this work was as following.

- Study to understand the characteristics of organic PV devices.
- Observation of device behavior with electrical and optical properties.
- Study to understand the physical characteristics of organic PV devices
- New design of OPV by introducing Ag at D/A interface
- Device fabrication of ITO/ CuPc/ Ag/ PCBM/ Al
- Study of Voltage and current characteristics of the device
- Study the effect of metal interlayer on OPV

Figurative flow of thesis



Summary

The world resources are going to be depleted day by day, the demand is increasing but not resources. The researchers are focusing on the renewable technologies; solar energy is the one of the most promising renewable source. Photovoltaic is the technology which is used for conversion of sun light in to electricity. There are two main types of PV technologies, inorganic and organic solar cell. Organic Photovoltaic (OPV) solar cells are emerging as a third generation of photovoltaic technology. The OPV provides assurance of a low cost solar photovoltaic solution and attracts important academic and industry research. In this work excellent electron donor CuPc and excellent electron acceptor PCBM materials were used for OPV characterization.

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Chapter 2

LITERATURE REVIEW

2.1 Solar cell

Solar cells are the semiconductor devices that convert light (photon) in to electrons or electricity.

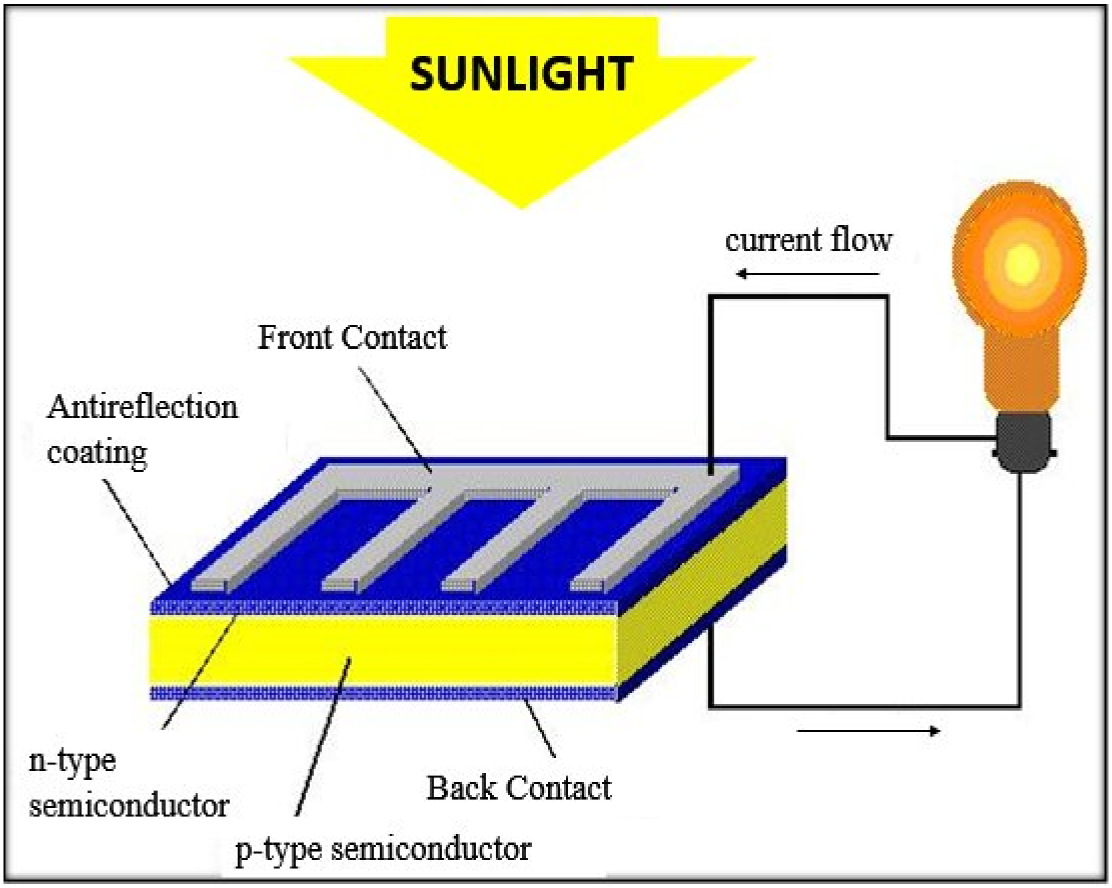


Fig. 2.1 Conversion of light to electricity

Fig.2.1 shows the simple conversion of light in to electrons or electricity but conversion phenomenon is not same in organic and inorganic solar cells the following section describes the brief introduction of organic solar cells.

2.2 Types of PV cells

Solar cells usually divided in to three categories.

2.2.1 1st generation solar cells

1^{st} generation solar cells include mono or polycrystalline silicon solar cells. This generation of solar cell is commercially dominant, currently covering 90 percent of solar cell marketplace [1]. Power conversion efficiency is the most general approach to calculate solar cell performance; PCE is the percentage of solar radiations that are coming from sun is converted to usable power by solar cell. Shockley measured the academic efficiency of several kind of single junction PV cell having 1.1eV band gap was 33% [2]. Kerr et al. measured theoretical efficiency with 90 micrometer thick single junction silicon PV cell was twenty nine percent [3].

Band gap of semiconductor is the one of reason for loss mechanism. The major portion of sun light that reaches the earth is infrared radiations, and mostly these are not sufficient to excite the electrons to conduction band. Lattice vibrations generated due to short wave length light (ultra violet) recognized the same like phonons. Thus a huge portion of UV light is lost as heat.

Mostly PV cells are fabricated using polycrystalline silicon and result in PCE of around 11-16 percent monocrystalline PV cells are formed through slicing of wafer using single crystal boule, this silicon lattice contains smaller amount of defects and usually higher efficiencies up to 25%. 1^{st} generation PV cells have comparatively higher efficiencies, reliability and lifetime. But their manufacturing cost is high and it is a big hurdle in the production of electricity from solar cell. While the production costs of first generation photovoltaic has reduced during last year's, silicon places a limit on reduction of price. The escalating order for microprocessors and further silicon-based devices does not assure good for the photovoltaic marketplace.

2.2.2 2^{nd} Generation PV Cells

The efforts to decrease material and manufacturing costs of PV devices linked with the usage of silicon, the focus of research since the last years on the improvement of more cost effective 2^{nd} generation solar cells (thin films) [4].

Thin film PV cells e.g. amorphous silicon, CdS/CdTe and Cu(In, Ga)Se 22 are fabricated using different deposition technique like sputtering, CVD, PVD, PECVD, usually have lower efficiencies than first generation solar cells. The highest efficiency attained using copper indium gallium selenide (CIGS) was 19.6% [5], that is not much less than the Power conversion efficiency of monocrystalline silicon PV cell. Major achievement in second generation solar cell is the reduction in fabrication cost and ability of quickly and easily fabrication then 1st generation solar cells. The reduction in manufacturing cost and easy fabrication techniques ensure a bright future of thin films solar cell in market.

2.2.3 3rd Generation PV Cells

3rd generation PV cells have different manufacturing designs it include Organic solar cells (OPVs), multijunction cells like 2nd generation cells, dye-sensitized sells (DSCs), and Bulk heterojunction solar cells etc. These emerging solar cells promise another approach at the manufacturing of cost effectively feasible solar energy. Polymers and small molecules are used in OPVs for the absorption of light and dye-sensitized PV cells depend on organic dyes to enhance photoexcitation. Organic PV cells and dye-sensitized consist of modest efficiencies approximately recorded PCE is 8.3% [5] and 10.4% [6] respectively. 3rd generation solar cells have unfavorable PCE however these solar cells are focus of research for researchers due to low material and production costs.

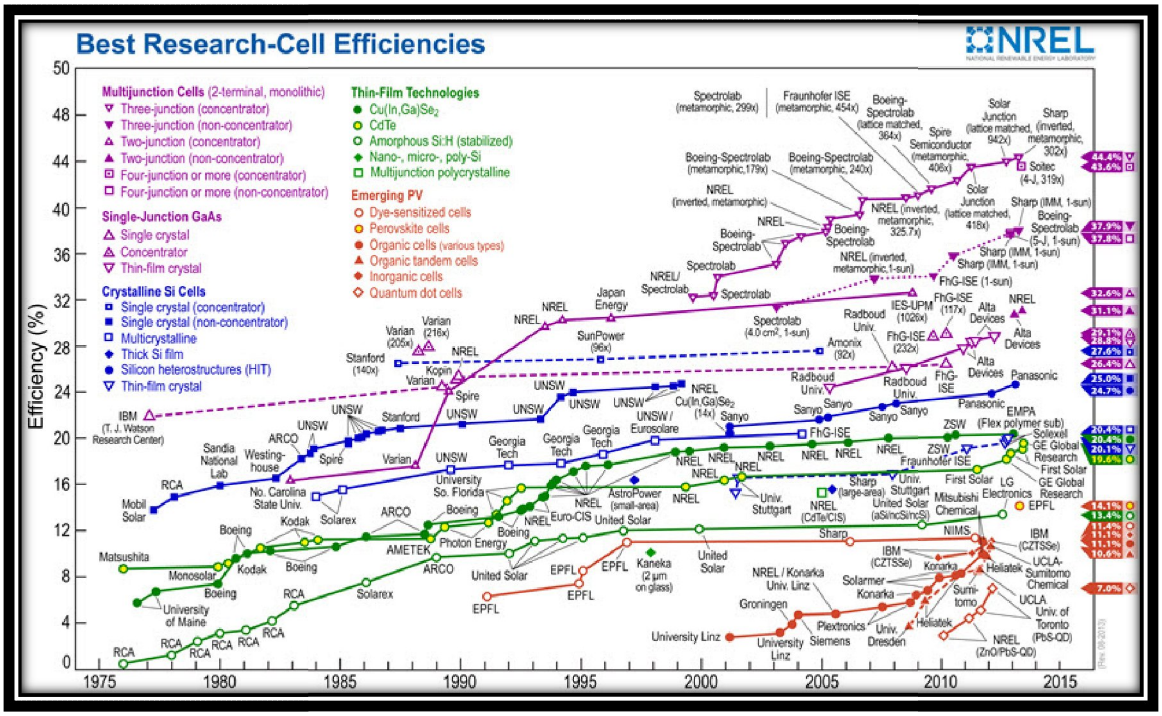


Fig 2.2 Recorded efficiencies of solar cells

Multijunction PV cells are priority of increasing efficiency to enhance the power to cost ratio. Multijunction PV cells are the type of tandem solar cells in which a number of cells stacked placed on top of one another. In multijunction PV cell every semiconductor exists in stack consist of a dissimilar bandgap to increase the segment of the solar spectrum that is captured by the PV module.

PV cells stack completely resembled to the solar spectrum can go above the Shockley and Queisser limit, academic efficiency limit approaches 66 percent. Higher efficiency solar cells manufactured in laboratories are stacked triple-junction PVs with PCEs above 40%.

2.3 Organic Solar Cells

OPV are the type of PV cells which use organic materials, either polymers or tiny molecules are used for light absorption and production of free electrons. During 1990 attention starts on OPV as Sariciftci et al. [7] described photo-induced charge transport among organic molecules in1992. Above the last 20 years researchers are taking serious interest in OPV for the reason that these solar cells have high possibility in cost reduction. Polymers can be manufactured on lower cost and since plastic's optical absorption coefficient is also high, very less amount of material is needed. These polymers easily dissolve in to the solvent; by different wet-processing methods e.g. spin coating and roll to roll printing these polymers can be deposited on substrate. The easy production processing allows low cost and large scale production. OPVs are the focus of researchers because they are free of rigid crystalline lattice and easily deposited on flexible surface.

2.4 Operational Principle of Organic vs. Inorganic solar cell

Excitons (electrons-holes pair) are rapidly generated upon absorption of light by semiconductor materials in Organic and Inorganic PV devices. Semiconductor is characterized by its band gap energy (E_{gap}), energy among (HOMO) highest occupied molecular orbital and (LUMO) lowest unoccupied molecular orbital.

Fig.2.3 shows the operation process of organic solar cell. Electrons are promoted from HOMO to LUMO if photon's energy is greater from the band gap and then excitons are generated. The E_{gap} for an inorganic solar cell is 1.4 eV at this value maximum amount of solar energy is utilized in generating excitons. [8] OSCs depend on a different method of electron-hole separation and there is not a single optimal band gap value that maximizes photon to exciton energy transfer. The OSCs band gap range from 1.7 to 3.0 eV and must be chosen sensibly to ensure sufficient exciton generation [9, 10, 11].

The method of electron-hole separation is the major difference among organic and inorganic PV cells. Within a p-n junction of Inorganic PV cells built-in electric potential is high enough at the p-n interface, free charge carriers produced virtually on the absorption of light. In organic solar cells excitons are electrostatically bound together due to the low dielectric constant of OSCs comparative to ISCs, a low dielectric constant indicates a large electrostatic enchantment among an electron plus a hole [12]. So to get over this electrostatic enchantment among electron plus hole an extra energetic force is required to separate these electron and hole in to mobile charge carriers. The charge separation occurred at the heterojunction among two organic semiconductors.

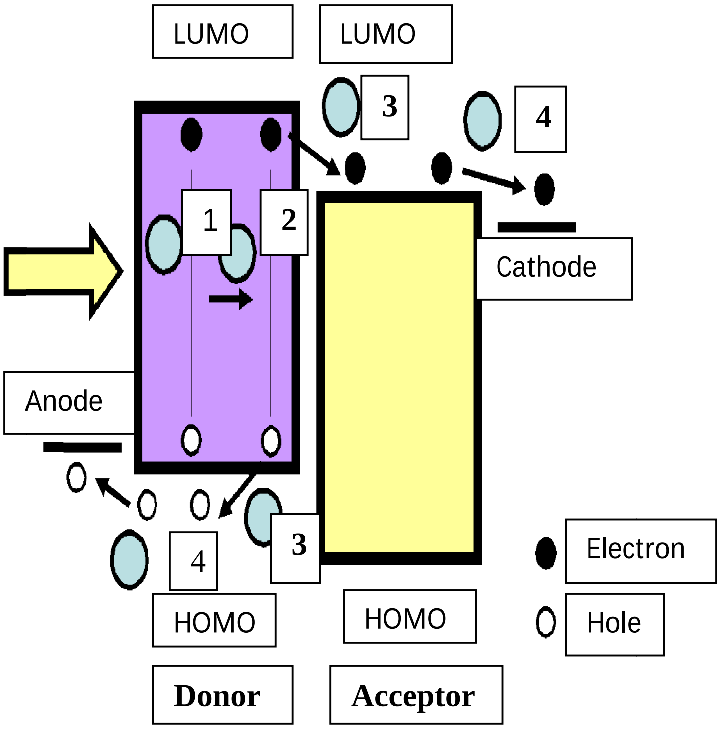


Fig. 2.3 the Operational procedure of the heterojunction organic photovoltaic devices, complete procedure counting: (**1**) the absorption of photon and generation of exciton (**2**) diffusion of exciton (**3**) dissociation of exciton (**4**) collection of carriers

2.5 Physics of organic solar cell

In a bilayer organic solar cell, a planar heterojunction consist of an active layer of two different semiconductor materials one is electron donor and other is electron acceptor. The energy level offset at the heterojunction is created due to the dissimilarity among HOMO / LUMO energy levels of two materials. Ionization energy of donor material is usually low, and electron affinity of acceptor material is high. Good donor as well as acceptor materials also has high charge carrier mobility and conductance. Offset at the heterojunction supplies the energy essential to overcome the electrostatic binding energy of the exciton.

The physics of organic solar cells involve the following factors these factors play an important role in performance of Photovoltaic devices.

- Absorption of Light
- Diffusion of excitons
- Transformation and separation of charges
- Collection of Charges

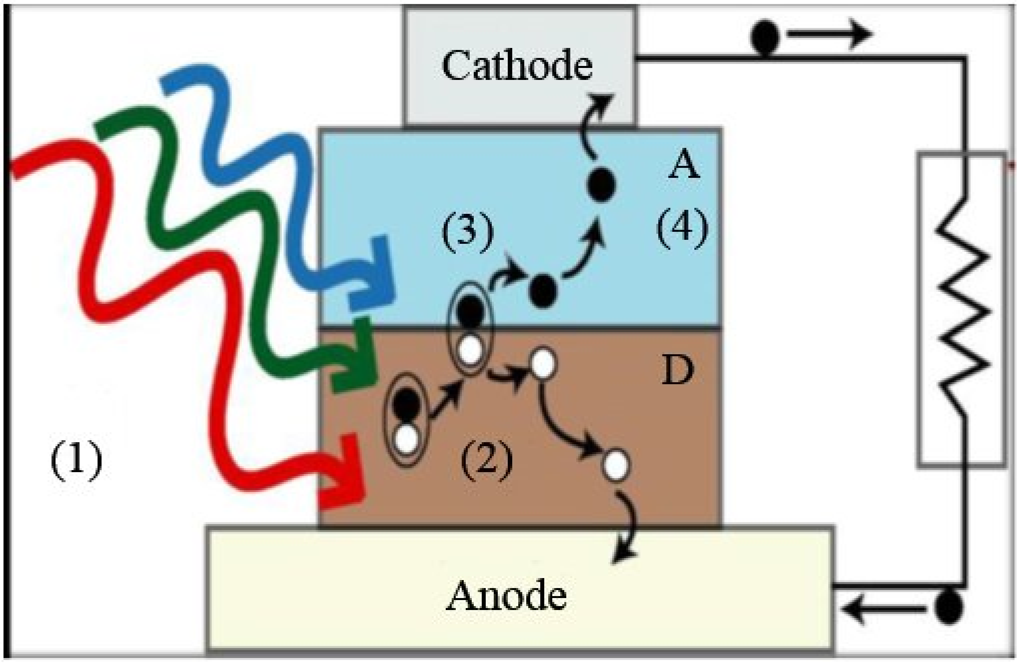


Fig.2.4 Cross-sectional diagram (not drawn to scale) of a bilayer OSC, where "D" denotes the donor and "A" the acceptor

2.5.1 Light Absorption

As the active layers thickness sufficient to absorb every one of the incident photons have limited internal quantum efficiencies (IQEs), therefore techniques are used to enhance the amount of absorbed light for a specified film thickness to increase the PCE of solar cell. Due to the lack of extended electronic states, organic materials absorption spectrum is thin as compared to the wide absorption spectrum of inorganic material. An extra dissimilarity with the majority of inorganic thin film PV cells is that optical interference property effects have to be considered to calculate absorption efficiency (η_A) as the OPV cells film thickness is comparable to the wavelengths of the sunlight, leading to standing wave effects that can change the optical absorption probability. The optical power density of absorbed light at a point x in the active layer of OPV can be described as [13].

$$?\,(?) = \frac{1}{2}??_0\,?\,\text{ŋ}\,[?\,(?)]^2 \qquad (2.1)$$

“C” the speed of light,

“$\square_0$” permittivity of vacuum,

“η" the real part for refractive index,

“E (x)” electric fields at position X

The electric field upon position x E(x) is usually measured with transfer matrix formalism. And UV-Vis spectroscopy is used for the measurement of transmittance as well as absorbance data of the required device which gives the total absorption measurements of the device or film. To increase the optical absorption, the film thicknesses should be adjust for a numbers of layers in the stack to spatially concentrate the light in different layers of OPV where it is powerfully absorbed [13, 14].

OPV active layer thickness is usually in the range of 50 to 250nm. This thickness is comparable to the absorbance length of OPV, particularly near the edge of the optical absorption spectrum at this point the devices are capable to preserve larger absorbed photon energy and light absorption is as a result suboptimal. For the improvement of PEC light trapping technologies are used these techniques improve the light absorption in the thin active layer. Performance of OPV can be increased by light trapping because internal quantum efficiency usually decreased with active layer therefore the thicknesses of active layers should be thin to attain higher IQE. Anti-reflecting coating is used to increase the absorption and air/substrate interfaces are used to reduce the reflections, and to trap photons in active layers a light confinement scheme is required.

The light trapping technologies that don’t need etching or patterning are well-suited with organic processing that are the main factors in recognizing practical light traps in Organic solar cells.

Agrawal et al. [15] described that the photocurrent can be enhanced up to 40% in power conversion efficiency of CuPc/PTCBI bulk heterojunction cell by introducing multilayer dielectric stacks between anode and substrate. These stacks work as an anti-reflecting coating layer and mirrors to include resonant cavity effect [16].

From the advantage of aperiodic structure, only four layers with TiO2 and SiO2 give the most favorable design for a CuPc/PTCBI bulk heterojunction solar cell. This design uses one-dimensional planar dielectric stacks lacking incorporating patterning or etching that could not be used with thin film organic processing.

2.5.2 Exciton diffusion

When a material layer or OPV device absorbs a photon an exciton is generated in organic molecules in a neutral excited state of molecules that polarizes the surrounding lattice. These generated excitons are diffuses in an organic solid and only a small numbers of excitons are able to reach donor/ acceptor junction these excitons have high probability to be dissociated in to charge carriers [17]. In planar bilayer organic photovoltaic cells excitons diffusion is the main efficiency blockage. The bulk hetero junction has mixed donor and acceptor solution therefore donor/ acceptor junction active layers give an efficient exciton dissociation to get rid of diffusion length blockage. Therefore the short diffusion length restricts the morphologies that can be used to construct efficient solar cell.

The diffusion length of excitons is measured experimentally by a steady-state or time resolved photoluminescence (PL) quenching, bimolecular photoluminescence quenching, photocurrent spectroscopy, or by fitting a model for the spectral shape of the external quantum efficiency to experimental data.

2.5.3 Charge separation

When solar cell absorbs photons it produced excitons then these excitons required separation in to charge carriers. Same time without an external field this is not an efficient process to separate exciton in bulk organic material [14].

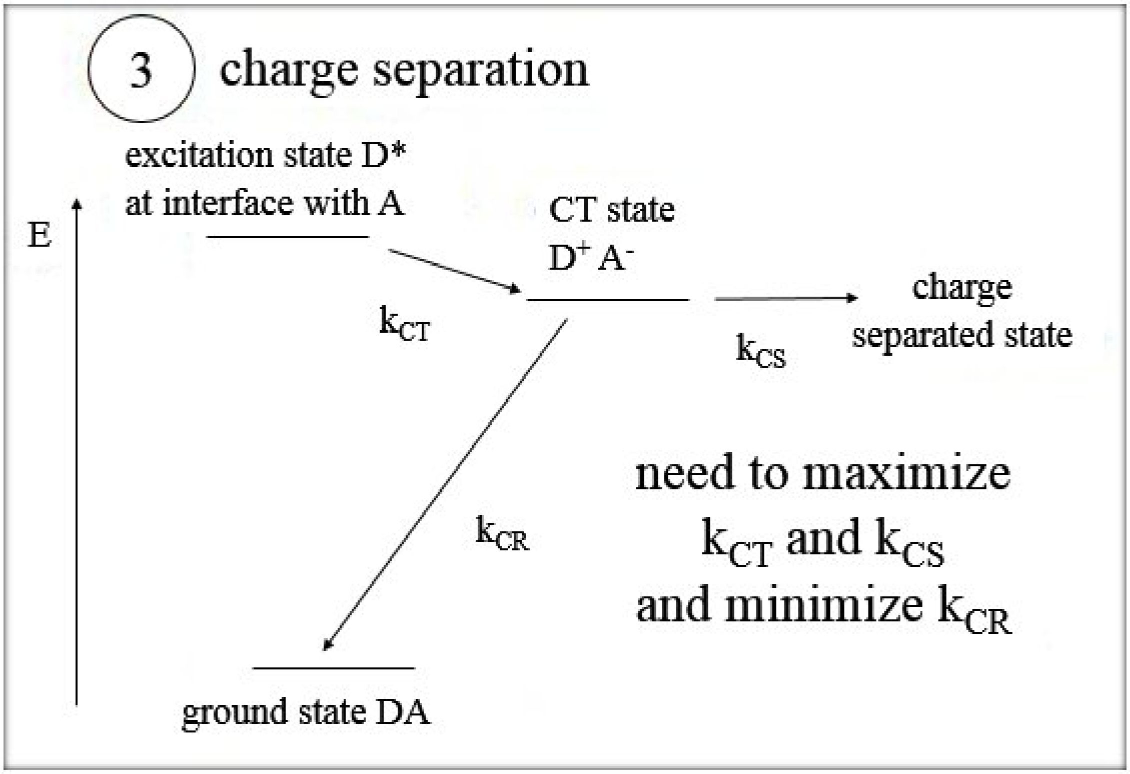


Fig. 2.5 Charge transformation and separation in OPV

The fig. 2.5 shows the process of charge separation and collection that is happening in the OPVs when excitons reach at the donor/ acceptor interface. Ground state is indicating lowest energy state of two components i.e. donor as well as acceptor. Assume that exciton is generated inside donor material. This exciton generated must reach the interface. Above the ground state at which the excitons exist is the energy of excitons. These excitons present at the interfacing point must get in to charge transfer state, the state in which electron must reach at the electron acceptor and at the same time hole transfer to the donor component, this is the stage that is called charge transfer state donor with +ve and acceptor with –ve charge. These +ve and -ve charges require to be move apart from each other, this state is called the charge separation state. So in organic solar cell charge transfer and charge separation both are necessary.

In this way it is necessary to fully separate these +ve and –ve charges for the generation of electrical current. In the above fig. charge separation and charge transfer states are nominated. Charge transfer state is the state at which both electron and hole are in front of each other and there is a chance of recombination which leads the excitons to ground state. If the same process is happen the loss in efficiency occur. Recombination is the key reasons for decrease in efficiency of Photovoltaic devices. The purpose of research for the researchers is to decrease charge recombination and increase the charge transfer and charge separation.

2.5.4 Charge collection

Distinctly from organic solar cells the inorganic solar cells have only single material to be used in device a negligible exciton binding energy at room temperature. The organic solar cells have different physic than inorganic solar cells because the exciton is strongly bonded. The donor and acceptor interface is needed in order to separate the generated exciton quickly. When the exciton is separated these separated electrons and holes must transfer efficiently towards the electrodes.

The collection of these charges scheme is shown in the following fig. 2.6.

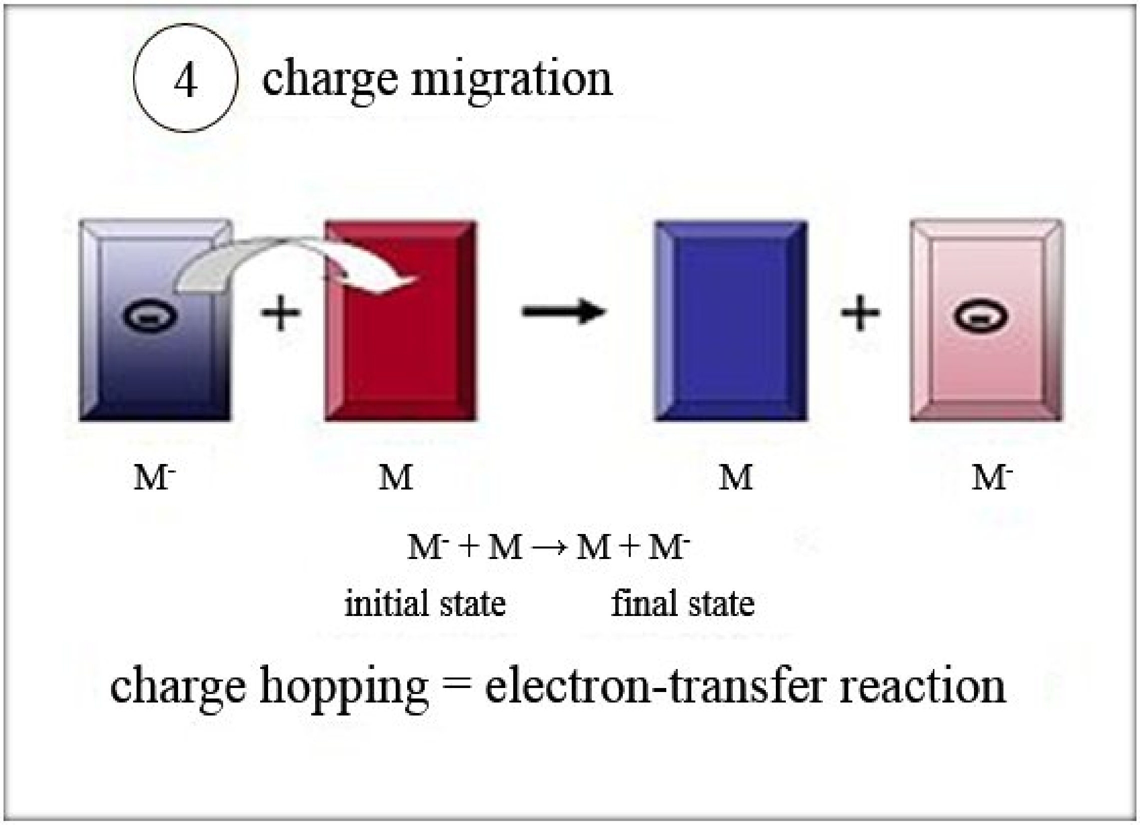


Fig.2.6 Migrations of charges

2.6 Energy Levels in Organic photovoltaic cells

In PV cells there are energy states or levels. These energy states are very important to be aware of the working principle of PV devices. There are two levels in organic solar cells first known as highest occupied molecular orbital (HOMO) other is lowest unoccupied molecular orbital (LUMO). HOMO level is around ionization potential of the molecule and LUMO level energy can be linked to the electron affinity of the molecule. The two terms electron affinity along with ionization potential are the characteristics of the entire molecule. HOMO and LUMO are the electron levels; these levels define the ground state and ionized state of the entire molecule. For the organic solar cell fabrication these states are very important for donor and acceptor material. When an electron takes energy and moves to the higher energy state then the dissimilarity among ground state and higher energy position is known as the ionization energy. And the concept of donor and acceptor is valid only if the ionization potential of donor material must be lower as compare to the acceptor material because donor is the material that can gives electron more easily.

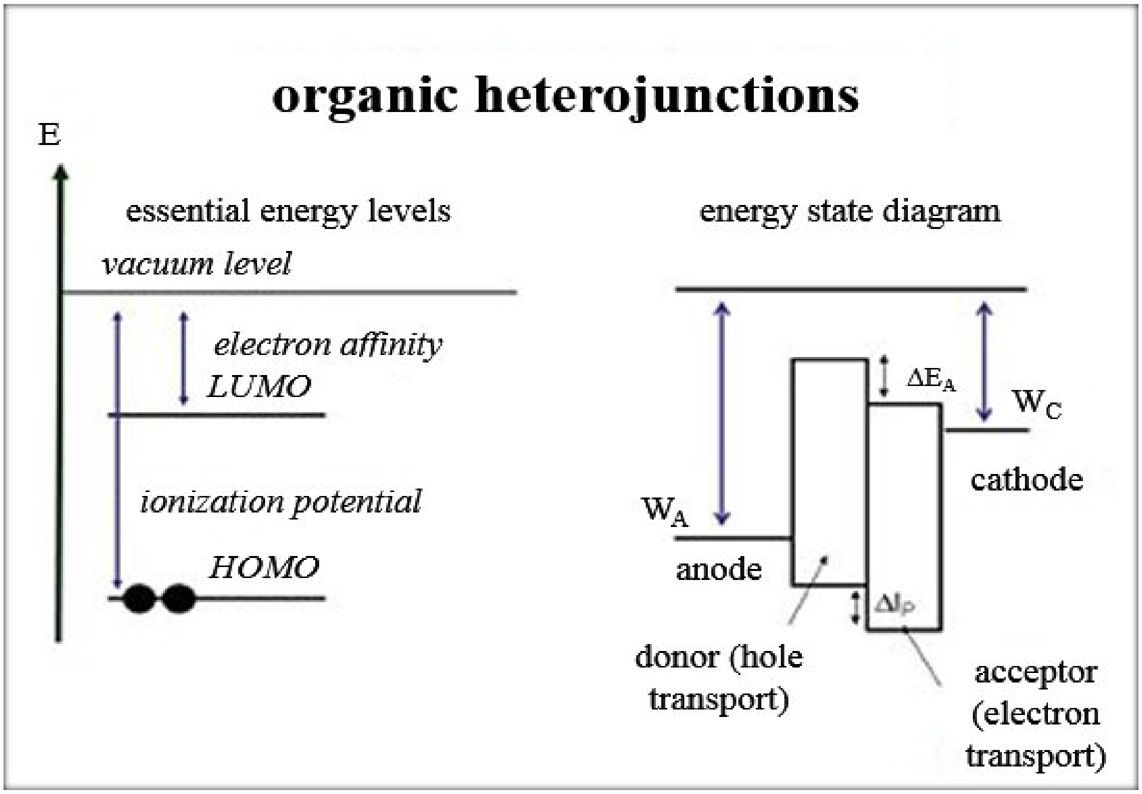


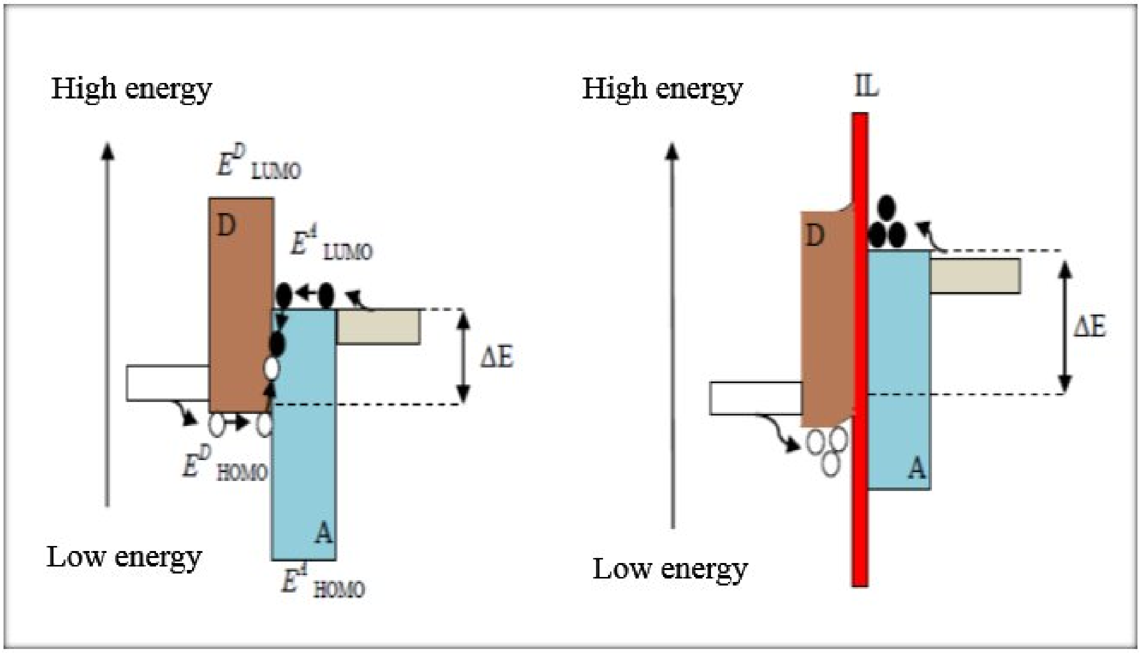
Fig.2.7 Energy levels of DA

And the fig. 2.7 shows that the ionization energy and the electron affinity of the donor are lower as compare to the acceptor material.

The open circuit voltage of device is described by the HOMO level of donor and the LUMO level of acceptor.

2.7 Insertion of interlayer and open-circuit (Voc) voltage

Under forward bias conditions organic solar cells present useful work, electrons are injected from cathode and holes from anode as shown in fig. 2.3. A bilayer cell consists of planer interface among donor/ acceptor material. Excitons travel towards heterojunction and they turn into highly concentrated and set up an electrochemical potential energy gradient for the photogenerated electrons and holes to diffuse away from the heterojunction and out of the device. The Voc is the theoretically maximum voltage at which a device can operate and occurred when the current in the device is zero at the similar time all the electrons plus holes recombine.



(a) (b)

Fig.2.8 Energy levels of organic solar cells

Fig. 2.8 (a) shows the injection of electrons as well as holes from cathode and anode under forward bias condition. The dissimilarity among HOMO of the donor as well as LUMO of the acceptor is ΔE, and Fig. 2.8 (b) shows the expected increment in ΔE due to insertion of interlayer because of band bending and decrease in charge carrier recombination.

The physical effects leading the Voc are still unidentified. It has been shown that the Voc of bilayer organic solar cells does not depend on the energy dissimilarity among anode/ cathode and vacuum level as it exist in Organic PV devices of single layer [18]. Hence research shows that the Voc is a function of the energy level difference at the heterojunction [11, 18]. That's why Voc directly increases due to increase in the energy difference of donor HOMO and acceptor LUMO

Insulating materials have been used as EBL (exciton blocking layer) such as bathocuproine used as exciton blocking layers to stop excitons from quenching at the acceptor-cathode interface, which improve the charge carrier collection at the cathode [10]. Lithium fluoride (LiF) has been used in the same way to reduce the electron injection hurdle at the acceptor-cathode interface [19]. In both cases, organic solar cell performance was improved. Liu et. al demonstrated in his study that the introduction of an interlayer material, a 5 Å layer of MoO3 positioned between the acceptor and donor, considerably increased the V_{OC} of a bilayer organic solar cells [11]. The authors finalized that band bending take place at the edges of the LUMO and HOMO and this increased the difference between donor HOMO and acceptor LUMO. Band bending is a fact that takes place due to a dipole formed between two materials, causing energy levels to shift.

2.8 Performance characterization:

Current-voltage (*J*-*V*) curves are helpful to examine the performance of organic Photovoltaic devices. A bias is applied to a device under illumination to study photo-response behavior. The V_{OC} is establish at the point at which the current is zero, and the J_{SC} (short-circuit current density) is found at the point at which the voltage is zero. The actual maximum operating power of the device is found by forming the largest possible rectangular area within the fourth quadrant. The efficiency of devices is usually characterized under AM 1.5 light.

The device efficiency (ŋ) can be measured under following equation (2.2).

$$? = \frac{?_{?\ ??} \times ?_{?\ ??}}{?_{?}} \tag{2.2}$$

Another important factor is the fill factor (FF) which is the ratio among maximum power send by device and product of Jsc as well as Voc shown in equation (2.3).

$$FF = \frac{J_{max} \times V_{max}}{V_{oc} \times I_{sc}} \tag{2.3}$$

By introducing an interlayer, it is assumed that the *J-V* curve will move to the right due to an increase in the V_{OC} as shown in fig 2.9. If the current is maintained at the same level earlier to the introduction of the interlayer, then the maximum power of the device will increase by an amount proportional to the increase in voltage.

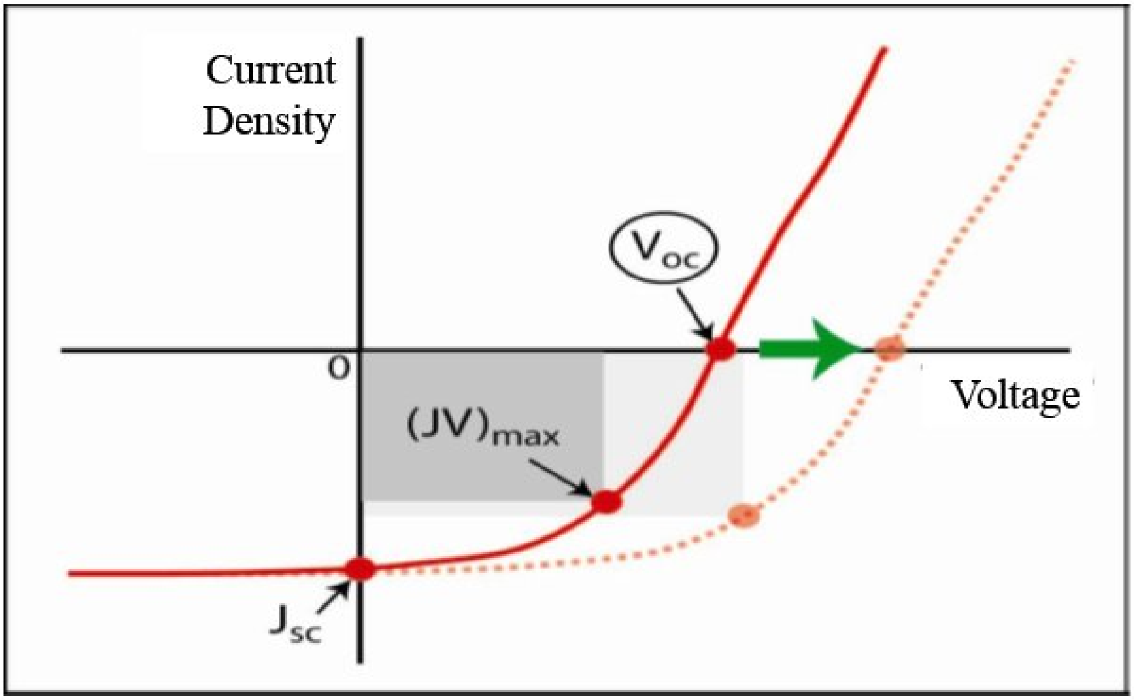


Fig. 2.9 I-V curve

Summary

There are different types of PV solar cells, mainly divided in to three generations 1st generation, 2nd generation and 3rd generation. 1st generations solar cells consist of inorganic solar cells 2nd generation consist of thin films and third generation are organic solar cells. OPV are the type of Photovoltaic devices that use organic materials, either polymers (macromolecules) or tiny molecules are used for absorption of light and production of free electrons. Organic solar cells have become serious attention for researchers because of high potential in cost reduction and other benefits over inorganic solar cells. The light conversion process consists of Light absorption, Exciton diffusion, Charge transfer and charge separation. The operation of organic and inorganic photovoltaic devices have different approaches, within a p-n junction of Inorganic solar cells the built-in electric potential is high enough at the p-n interface that free charge carriers are generated virtually upon absorption of light. In organic solar cells excitons are electrostatically bound together due to the low dielectric constant of OSCs comparative to ISCs, a low dielectric constant indicates a large electrostatic attraction among an electron and hole. So to get over this electrostatic attraction among electron and hole an extra energetic force is required to separate these electron and hole in to mobile charge carriers. The charge separation occurred at the heterojunction among two organic semiconductors.

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Chapter 3

PROPOSED SOLUTION/ METHODOLOGY

3.1 Designs of Organic Photovoltaic devices

Researchers are working to find the best green energy solution for this world in this way they find solar energy, this energy can be obtained using inorganic materials and organic material due to expensive production of inorganic solar cells the researchers are focusing on deficiencies of organic solar cells e.g. short diffusion length, recombination, etc. To get rid of these issues the scientist invented different construction structure to get better efficiencies.

Some structural designs of organic solar cells are given below.

- Single layer
- Bilayer
- Bulk hetero junction
- Discrete heterojunction
- Graded heterojunction
- Tandem solar cell.

3.1.1 Single layer organic Photovoltaic device

The category of PV cell in which only Single material layer is used is the simple form of organic PV device. Fabrication of simple organic PV device is finished by introducing an organic material sandwich between two metallic electrodes. The device structure is shown in the following fig. 3.1

The fig. 3.1 shows that the organic material is sandwich between the usually high function electrode ITO and a low function electrode Al or other. The solar cell characteristics can be determined with the selection of these electrodes. The device behavior can be analyzed with work function. The work function difference of the electrodes generates the electric field to separate the excitons. The difference between the vacuum level and the Fermi level of the material is known as work function.

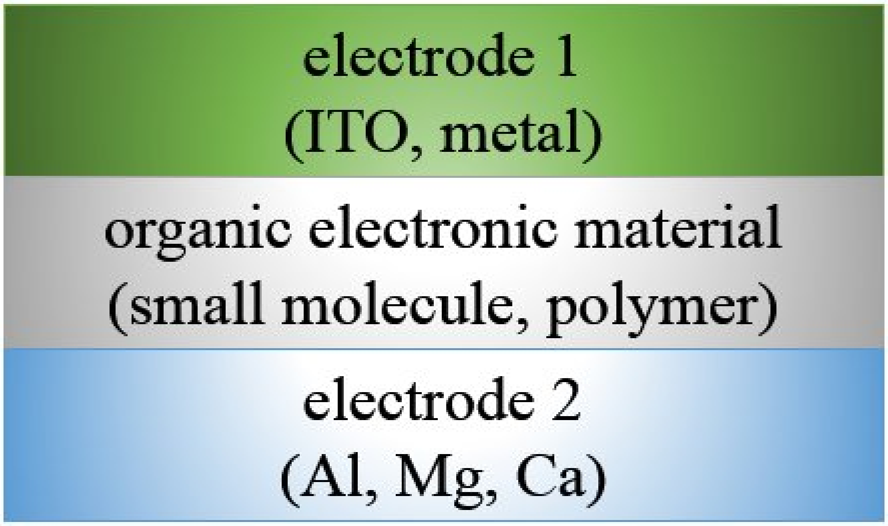
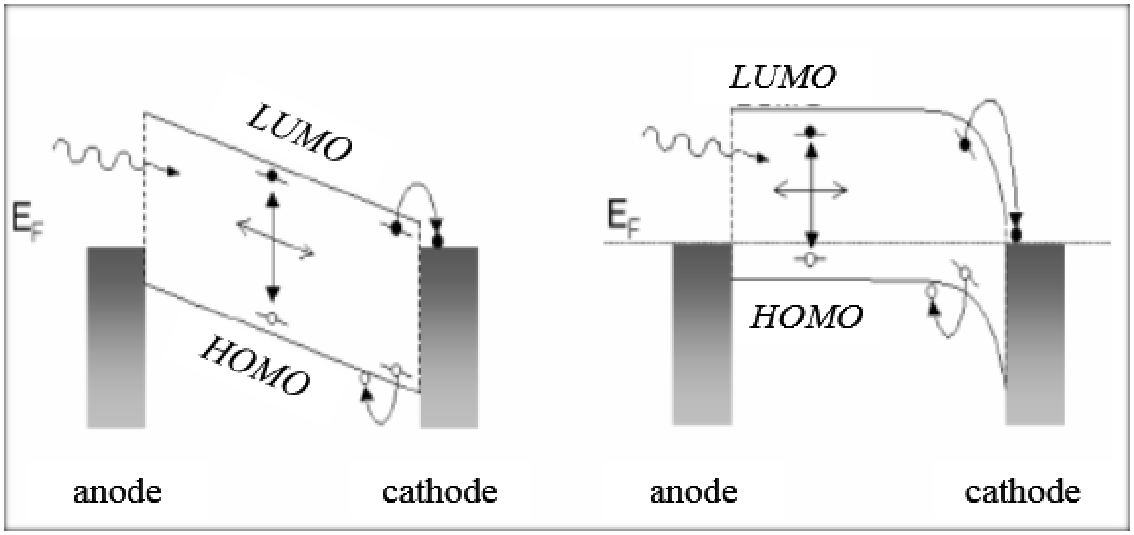


Fig. 3.1Ssingle layer organic solar cell

Upon the absorption of light the energy of excitons are increased and these excitons are promoted to the LUMO level and holes are generated in HOMO level. The electric field is set up between the electrodes because of the dissimilarity of work function. In the depletion region of schottky barrier the excitons are separated.



(a) (b)

Fig. 3.2 The band illustration of single layer organic PV cell (a) metal insulator (b) Schottky

These solar cells have lower frequencies, QE (quantum efficiency) below 1% and CE (conversion efficiency) below 0.1%. The lower efficiencies are because of inefficient separation of excitons. The generated electric field is not enough to separate these excitons, therefore the generated electron sand holes recombine before contact to the electrodes.

3.1.2 Bilayer organic photovoltaic device

The type of organic PV cells, that consist of two organic layers of different material are sandwich among two electrodes. The following fig. 3.3 shows its constructional design.

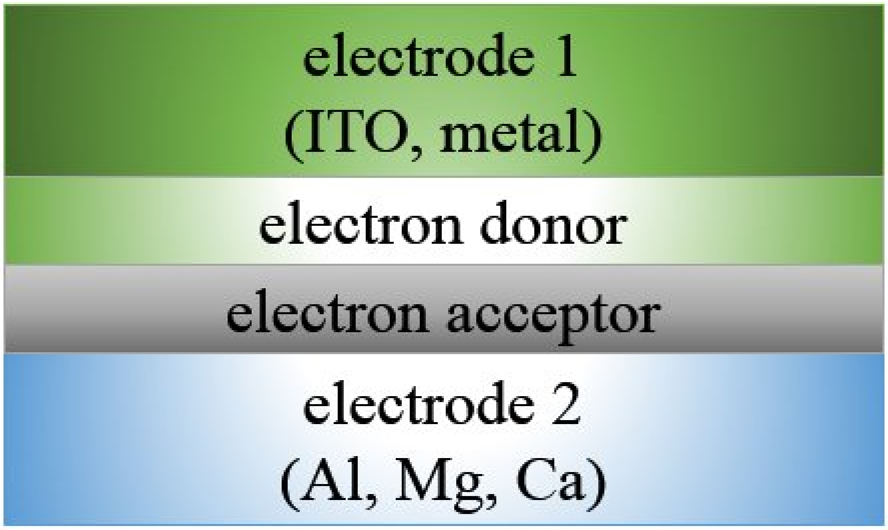


Fig. 3.3 Bilayer organic solar cell

This kind of organic PV cell is also known as planar donor/ acceptor heterojunction organic solar cell. The interfacing point of donor and acceptor acts for the separation of excitons in to charge particles. Both the donor and acceptor are chosen with different ionization potentials and electron affinities. And electrostatic force is created because of these differences at interface. The donor and acceptor are chosen with larger difference. So in this type of devices the electrostatic force is stronger to break excitons in to charges as compare to the single layer organic solar cells. The acceptor material is chosen with higher electron affinity and ionization potentials as compare to the donor material.

When the donor material absorb light the electrons of donor material are get excited and move from HOMO to LUMO and creates excitons. If the acceptor material is near to the generated exciton then this exciton can migrate towards the acceptor material and dissociate upon donor/ acceptor interfacing point. The transfer of exciton is occurred if ionization energy of excited state of donor fulfills following relation.

$$?_{?*} - ?_{?} - ?_{?} < 0 \qquad (3.1)$$

"$?_{?\,*}$” The excited state Ionization potential of donor

"$?_{?}$" Acceptor material’s electron affinity

"$?_{?}$" Affective columbic interaction

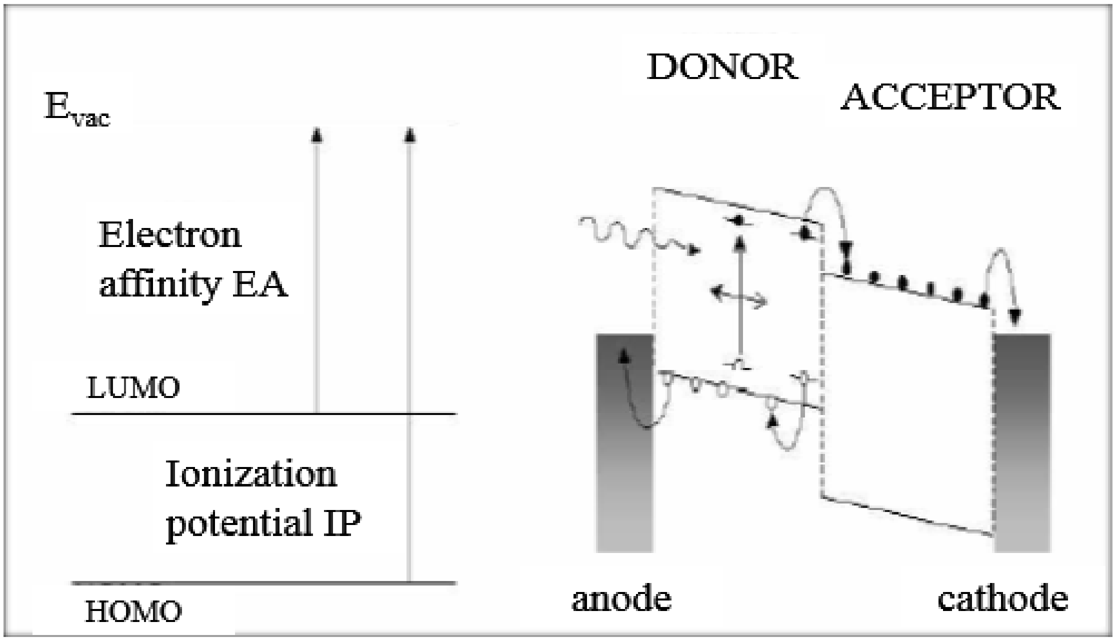


Fig. 3.4 Band diagram of organic material and bilayer device

Above diagram shows that higher voltage can be achieved from this device. The energy of excitons increased when material absorb photon and moves to the higher energy level, then charge separation occur at the planar interface decrease the energy of charge carriers that was received from absorption of photon. The figure shows that the high energy achieved is the dissimilarity among the LUMO of acceptor and HOMO of donor. Energy difference as explain above is known as effective band gap of the organic material.

After separation of excitons at the interfacing point of heterojunction, the electrons plus holes shift towards external circuit through n type and p type material respectively. In this way the recombination rick is reduced as the holes and electrons are efficiently separated from one another. The recombination occurs is only due to the trap densities. The electrons and holes are absorbed in the positions where these traps generated. Short exciton diffusion length is the main problem in these devices. 10nm is the approximate diffusion length of excitons therefore the effective separation of excitons depends on the thickness of the layers that must be in the range of this diffusion length. But to absorb the sufficient photons the minimum thickness of the organic material layer should be 100nm. But at this thickness only a limited percentage of excitons are able to reach the interface point.

3.1.3 Bulk heterojunction organic solar cell

The problem of short diffusion length in which only limited numbers of excitons are able to reach the interfacing point is overcome in bulk heterojunction design of organic solar cell.

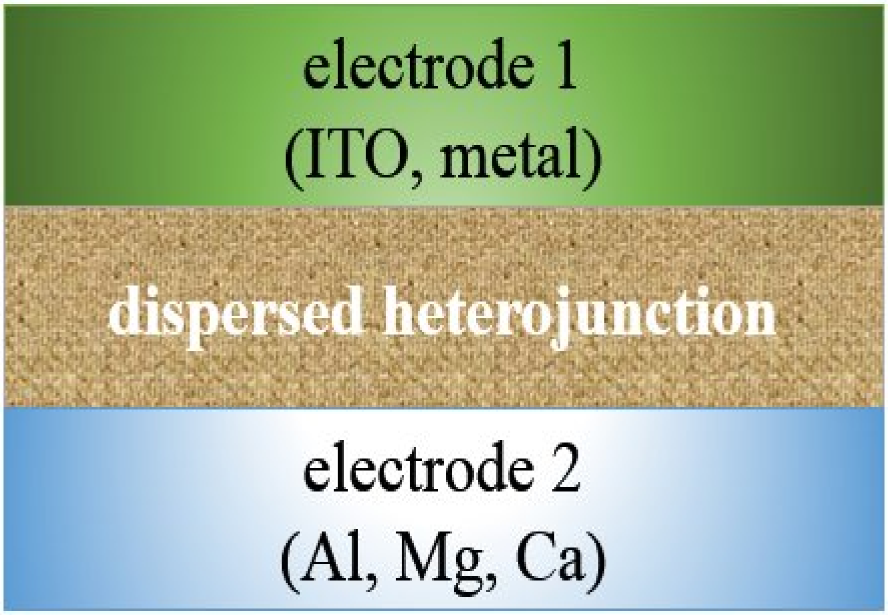


Fig. 3.5 Bulk heterojunction organic solar cell

The fig. 3.5 shows the diagram of bulk heterojunction organic solar cell in which polymer blend (donor and acceptor mixed material) is sandwich between two electrodes. The most of the excitons that are generated in the blended solution are able to reach the donor/ acceptor interface if the length of the blend is equal to the diffusion length of excitons. This design of organic solar cell leads to the proficient separation of excitons. The holes are collected at anode while travelling through acceptor to donor material and electrons are collected at cathode while travelling in opposite direction. The design of bulk heterojunction is same as in the bilayer structure with respect to donor/ acceptor concept, but in bulk heterojunction interfacial area is increased where exciton separates. The performance of this type of solar cell is highly dependent on the nano morphology of the bled because the donor and acceptor phases have to form an interpenetrating and bicontinuous network for the shipping of charges.

Generated excitons are now everywhere inside the bulk. These generated excitons are nearer to donor/ acceptor interfacing point therefore dissociation of excitons is efficient and separation occurs all over in the bulk layer.

The dashed lines are showing the energy level of donor material and the dotted lines are showing the energy level of acceptor material. Selection of electrode material should be in order to consider the energy level of acceptor and donor that the work function of 1 electrode is nearer to the LUMO of acceptor along with other electrode makes a good contact with HOMO of donor. Dissimilarity among the LUMO of acceptor and HOMO of the donor defines the Voc of device.

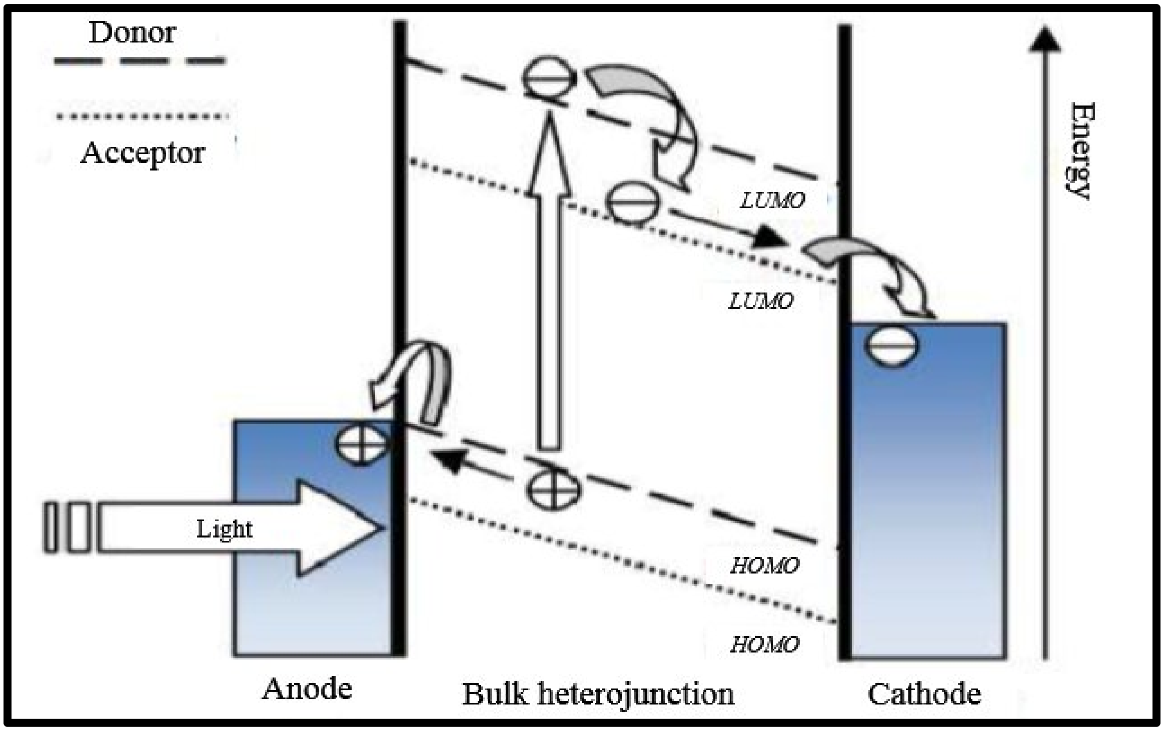


Fig. 3.6 The schematic diagram of bulk heterojunction solar cell

Different materials have been used as the sandwich layer in the bulk heterojunction solar cells. Shaheen et al. noted the higher efficiencies using bulk hetero junction he indicate that solvent has major effect on the show of bulk heterojunction of solar cell [1]. The 2.5% efficiency was achieved by optimizing processing circumstances. The achieved efficiency of 2.5% was bulk heterojunction efficiency using PCBM and MDMO PPV as acceptor and donor material respectively. After fabrication annealing of the device result in higher efficiencies as the PCE of 3.5% was achieved using P3HT and PCBM blend.

3.1.4 Discrete heterojunction solar cell

The design of organic solar cell in which a three layer stack is used which contains two layers of acceptor and one layer of donor. The efficiency of 8.4% was achieved. This design produced higher Voc, higher absorption in visible spectrum and higher short-circuit current. Quantum efficiency was achieved about 75% in the range of 400 to 720nm wavelength with Voc of 1 V.

3.1.5 Graded heterojunction organic solar cell

In this type of solar cell design both acceptor and donor are mixed in such a way that the gradient is regular. This structural design merges the short electron travel distance in the isolated heterojunction with the advantage of the charge gradient of the bilayer technology [2].

3.1.6 Tandem organic solar cell

This is the new design of organic solar cells to get higher Voc, in this design two or more cells are deposited in series on the same substrate and separated by an ultrathin metal layer is called tandem solar cell.

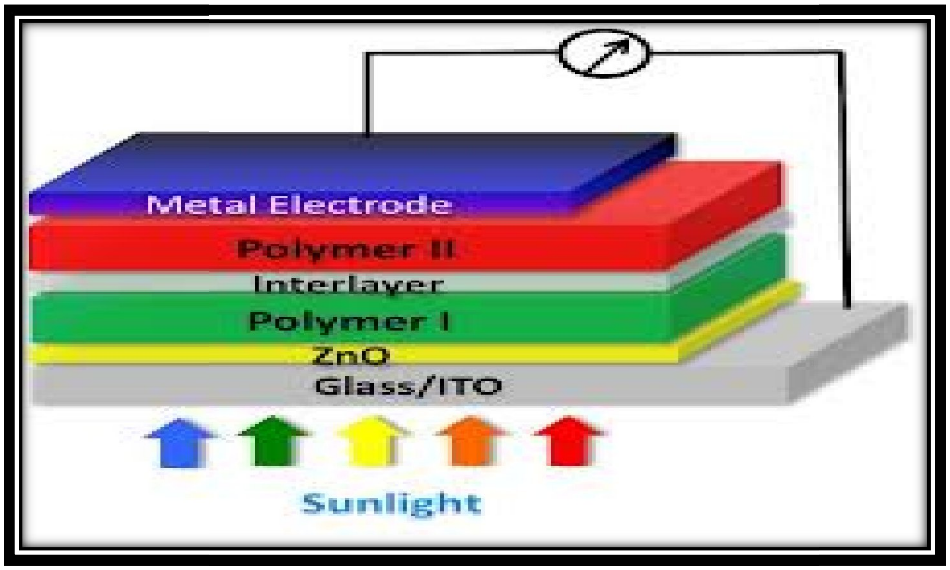


Fig. 3.7 Tandem solar cell

The Fig. 3.7 shows that in tandem solar cells two cells are separated by interlayer. The two cells in a series of tandem solar cell allow Voc to increase twice as compare to the single junction solar cell. Excitons are generated in both PV cells after the absorption of photons. When the dissociation of excitons occurred at the interfacing point of donor/ acceptor material, the holes from the front Photovoltaic device and electrons from the back photovoltaic device are collected on adjoining electrodes. To avoid build-up of charge inside the cells, electron from the front Photovoltaic device and hole from the back Photovoltaic device diffuse to the metal nanocluster layer at this stage these electrons and holes recombine. This design is beneficial to make a thin individual OPV cell to get maximum numbers of excitons at the interfacing point of donor and acceptor to increase the photocurrent. Whereas the hole device thickness should be enough to get the large absorption efficiency. The power conversion efficiency is increased in tandem solar cell as compare to single cell 1.1% to 2.5%.[3].

3.2 Deposition and Characterization Techniques of Organic solar cells

There are some depositions and characterization techniques of organic solar cells these techniques are describes one by one under following.

3.2.1 Organic Film

An organic film is a coating of a material with width of nanometers. Key utilization of organic films is the production of semiconductor devices plus the study of several properties of materials like electrical, optical, structural *etc*. Manufacturing of Organic solar cells based on caliber of deposited films.
The excellence of thin films based on the following features.

- Film Deposition method
- Substrate's Material
- Rate of film deposition
- Temperature of Substrate
- Control of contaminants (back ground pressure/vacuum) [4]

Organic film expertise depends on three fundamentals; fabrication, film characterization and its application. Organic films are helpful for the study of various properties of materials *e.g.* structural, electrical, optical *etc*. These all factors depend on the deposition methods. A number of deposition techniques exist all these deposition techniques of films have various advantages plus disadvantages; selection of suitable method for correct use is of key importance. Films of any material can be deposited by a variety of methods and then compared with each other after that suitable technique is applied to optimize the necessary device. In the same way organic films grown on unlike substrates having dissimilar properties (*e.g.* adherence, impurity diffusion *etc*) are also well thought-out in optimizing a device.

3.3 Technologies used for film deposition

The numbers of processes exist for deposition of organic films however fundamentally each process has 3 same steps film deposition.

- Formation of the depositing film species
- Transformation from source toward substrate
- The Deposition of film upon substrate and successive growth of film.

All above mentioned steps can be totally detached from one another or can be superimpose on each other based on the technique in concern [5].

A number of deposition types exist for depositing plus fabricating organic films however usually we break up these into two groups [6].

- The Chemical vapor deposition (CVD)
- The Physical vapor deposition (PVD)

3.3.1 Chemical Vapor Deposition

CVD is a method in which the substrate is open to the elements of one or more volatile precursor, these precursors reacts with the surface of substrate and creates the required film [5]. The method is frequently used in the semiconductor industry to fabricate organic films. In this deposition technology, the solid substance is vaporized moreover a chemical reaction takes place in surrounding area of a hot substrate. CVD method is extremely valuable in industry of semiconductor materials. Major benefit of this technique is of comparatively lesser cost plus high rate of deposition.

3.3.2 Types of CVD

There are number of different techniques of CVD these are given below. These techniques are usually differing in the way by which chemical reactions are initiated.

3.3.2.1 Operating Pressure

The types of CVP are classified by the difference in their operating pressure.

a) **The Atmospheric Pressure CVP**

In this technique the process of deposition is carried out at atmospheric pressure and known as APCVD. The worth of these deposited films are lower than those of the low pressure manufactured films.

b) **The Low pressure CVP**

In this type of CVP process sub atmospheric pressure is utilized.

c) **The Ultrahigh vacuum CVP**

The type of CVP which based on a very low pressure (Very high vacuum) more or less lower than 10^{-6} Pa is used.

3.3.2.2 Physical characteristics of vapor

These types of CVD are classified by physical characteristics of vapors
These types are explained one by one following.

a) **Aerosol assisted CVD**

In this type of method precursors are transferred toward substrate with the help of liquid/gas spray that can be produced ultrasonically. The ASCVD technology is appropriate for use by means of non-volatile precursors.

b) **Direct liquid injection CVD**

In this process of CVD the precursors exist as liquid form. Liquid solutions are inserted in to vaporization chamber on the way to injectors (usually car injectors). The precursor vapors are then transferred to substrate same as in classical chemical vapor deposition. DLICVD is appropriate to utilize on liquid and solid precursors. High growth rates can be achieved using this process.

3.3.2.3 Plasma Method of CVD

a) **Microwave plasma-assisted CVD:**

Plasma-Enhanced CVD:

Precursors are transformed to plasma prior to deposition on the substrate known as plasma-Enhanced CVD.

b) The Remote plasma-enhanced CVD:

Both the remote plasma enhanced and plasma enhanced CVD techniques are same excluding that wafer substrate is not directly in the plasma discharge section. Eliminating wafer from the plasma region permits processing temperatures decrease to room temperature.

3.3.2.4 Atomic Layer CVD:

In AL process of CVD the layered crystalline films are prepared by deposition of successive layers of unlike substances on the substrate.

3.3.2.5 Combustion CVD:

The process of CCVD is a technique based on open atmosphere and flame for high quality film and nanomaterial deposition.

3.3.2.6 Hot filament or catalytic CVD:

HFCVD or CCVD is the process in which hot filament is used to chemically decompose the source gases [7]. The temperature of filament and substrate are independently controlled, it allows colder temperatures for good absorption at substrate and higher temperature is essential for decomposition of precursors to free radicals at the filament.

3.3.2.7 Hybrid Physical CVD:

In this process chemical deposition of precursor and solid source vaporization both concerned.

3.3.2.8 Metal-organic CVD:

In this process of CVD metal-organic are used as precursor.

3.3.2.9 Rapid thermal CVD:

The process in which heating lamps or other techniques are used for heating up the wafer substrate quickly is known RTCVD.

3.3.2.10 Photo-initiated CVD:

In this process chemical reaction is stimulated using UV light. Same like plasma processing.

3.3.3 Advantages of CVD:

There are some benefits in CVD.

- High dense and pure materials can be constructed using chemical vapor deposition.
- In CVD at high deposition rate the regularity and adherence is high.
- Throwing power of CVD is good that's why it can be used for complex shape coating.
- Crystalline plus surface morphology can be controlled with CVD.
- CVD products orientation can be controlled through handling its parameters. It has lower processing cost.
- A huge spectrum of material can be deposit through CVD e.g. metal, oxides, nitrides and compound semiconductors.
- Lower deposition temperature is needed in majority of CVD process.

3.3.4 Disadvantages of CVD

There are some drawbacks of CVD these are listed below.

- The deposition process of CVD is complex and dangerous because materials used in CVD are toxic, corrosive, flammable or explosive.
- CVD deposition rate is different that's why deposition of multi component materials using multi source precursors is difficult.
- Manufacturing cost of devices is high in CVD process because of sophisticated reactor, ultra high vacuum CVD, photo assisted CVD and plasma assisted CVD and etc [8].

3.3.5 The Physical Vapor Deposition (PVD)

This process of physical vapor deposition based on atoms or group of atoms are driven out from a solid or liquid source then go to a vacuum chamber to set down on substrate physically. The rate of PVD based on pressure of system, source and substrate space and temperature of substrate. This technique of deposition is broadly utilized in manufacturing of the items containing semiconductor devices along with coated cutting tools used for metal work.

PVD techniques can be expressed in two major types.

a) Sputtering

b) Vacuum Thermal Evaporation

3.3.5.1 Sputtering

As soon as some particle with high speed hits on a targeted place and throw out the atoms from that surface is known as sputtering. In this type of technique, atoms are driven out from surface of a solid with bombardment of higher energy particles. The sputter output (sputtering rate) is described as "the average number of atoms driven out from target surface for each incident ion". Sputter output based on factors as incident angle, masses, energy of ions as well as targeted atoms. Math of sputtering can be expressed in the following equation [9].

$$y = \frac{N_e}{N_i} \qquad (3.2)$$

"Y" sputtering output or yield

"N_e" quantity of expelled atoms

"N_i" amount of incident ions

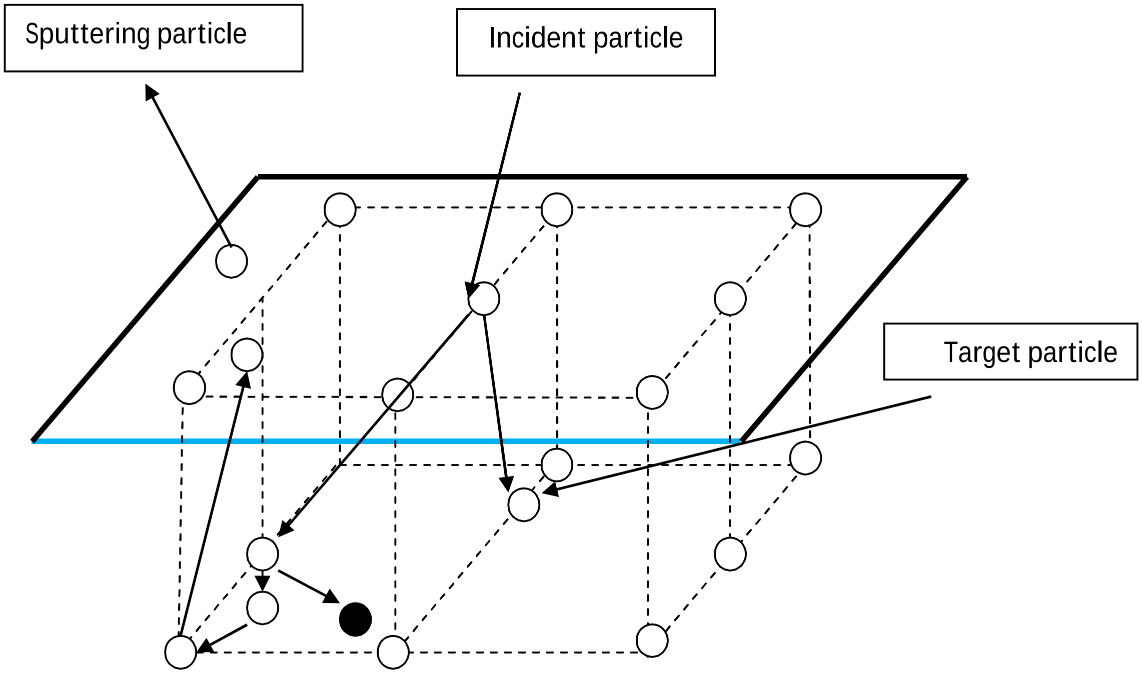


Fig.3.8 Sputtering process

Sputtering elements have high kinetic energies than thermal evaporated particles. Sputter deposition is the technique in which source material (target) is mounted appropriate to substrate in vacuum chamber evacuated with the base pressure $10^{-6} – 10^{-10}$ Torr based on conditions. Negative potential of among 0.5 – 5 kV is applied on target to begin positive ion bombardment although the substrate is grounded. Source material is transformed to vapors as the positive ions are bombarded on it with physical momentum exchange. Momentum is elastic as well as it is clear from fig. 3.8 that sputtering take place further than single binary momentum. For the sputtering of metals, generally DC sputtering (known as diode or cathode sputtering) techniques are used as well as for sputtering of insulators, RF potential is applied to target.

3.3.5.1.1 DC sputtering:

In DC sputtering, plate of material to be deposited is finished as cathode. At low pressure, as the cathode cover is very large and ions cannot get in touch with target easily and as a result deposition rate decrease. When pressure is increased at fixed voltage, more ions are produced and bigger current flow that deposited extra atoms on substrate affectively. But if pressure is become high, the collision between atoms increases and deposition efficiency of the atoms upset. Usually, the deposition rate is proportional to the current and inversely proportional to the distance between electrodes [10].

3.3.5.1.2 Radio Frequency Sputtering:

RF sputtering (also known as AC Sputtering) is used to deposit insulating thin films. In this procedure, energetic RF waves produce +ve ions in the inert gas. These ions shatter target material into small pieces that starts to coat substrate surface.

3.3.5.1.3 Reactive sputtering:

In this process of sputtering compounds are deposited on substrate by sputtering from metallic targets in the occurrence of a reactive gas generally mixed with inert gas.

3.3.5.1.4 Bias sputtering:

In this technique, electric field is applied close to substrate to differ the flux and energy of incident charged particle by applying -Ve DC or RF bias to substrate. The voltage applied to the target is 1000-3000 V and bias voltage is -50 to -300 V.

3.3.5.1.5 Magnetron sputtering:

In this process of sputtering “magnetic field shifted to the electric field at the target surfaces is known as magnetron sputtering”. In this method, electrons work under the collective effect of electric and magnetic field. Here more current is drained and rate of deposition increases around 1 μm per minute. In a typical magnetron sputtering, pressure is kept at few milli-torrs and atoms move in the ballistic approach to deposit on substrate [11].

3.3.5.2 Vacuum Thermal Evaporation:

In this technique of thermal evaporation, the material used as source is energized thermally in existence of vacuum as of source to target (substrate). In this technique following points involved.

- The Sublimation
- Vapors movement source toward substrate
- Vapors condensation on substrate
- Vapors arrangement on surface of substrate [6]

High vacuum is required to sublimate (evaporate) a material, normally diffusion pumps and rotary are used to decrease the pressure as of the vacuum chamber.

Vacuum levels divided as following:

Lower vacuum = 760 -25 Torr

Medium vacuum = 25 -10^{-3} Torr

High vacuum = $10^{-3} – 10^{-6}$ Torr

Very high vacuum = $10^{-6} – 10^{-9}$ Torr

Ultra high vacuum < 10^{-9} Torr

Vacuum thermal equipment includes heating source and this source is heated electrically until material begins to evaporate at its sublimation point. The substrate temperature is kept very low as compare to the source. Because these vapors are condense on the surface of substrate. Vapors can be stopped using shutter when material is not sublimate up to essential rate or thickness has been deposited. Usually $10^{-5} – 10^{-7}$ torr vacuum is used in thermal evaporation system. The mean free path of vapors increases due to this low pressure and the vapors pass through in a directly straight line as of source toward substrate. The film formed with this technique is of best worth and well defined with preferred orientation.

Thermal evaporation can be carried out with these three under lying techniques.

- Heat Resistive Method.
- Electron Beam Method.
- Close-Spaced sublimation. [6]

3.3.5.2.1 The HR Thermal Evaporation

The HR thermal evaporation is a method in which electrical energy is converted to heat energy using highly electrical resistive evaporent in a vacuum chamber. Because of low pressure in chamber, materials evaporation occurs, sublimated without difficulty. In this method tungsten, molybdenum or tantalum is used as evaporent source just like a coil or boat. The selection of this evaporent boat or coil depends the type of material to be used for evaporation *i.e.* Non reactive with the material. Substrate temperature can be changed by changing heater current located just above the substrate holder. Quartz crystal is used to measure the thickness of the film.

(a) Quartz Crystal (b) Coil (c) Coil

Fig. 3.9 Components of HR

High vacuum is attained with the help of Rotary and diffusion pumps. The substrate temperature is managed by changing current when vacuum of required level is achieved. Evaporation rate depends on the source material’s temperature which is directly controlled by changing current with the help of heating element. We know as the current passes through a resistive substance, electric energy converted to heat and temperature of the substance boosts. Mathematically the relation between current temperatures can be explaining using the following equation.

$$? = ?_?[1 + ?(? - ?_?)] \qquad (3.3)$$

R, at high temperature T resistance

R_o, at low temperature resistance T_o

α, indicates coefficient of temperature.

The resistance, voltage and current relationship is described according to the Ohm's law

'V' indicates voltage moreover 'I' indicates current.

Once getting the necessary rate of deposition after that shutter is moved moreover deposition begins after getting the mandatory thickness again the shutter is placed and deposition stopped. Source terminal power is slowly decreases to end the evaporation. The system is switched toward cool down to attain temperature of substrate equal to the temperature of room if required. It is compulsory to guard film as of atmospheric consequence like oxidation.

The diagram of HR system is shown as under.

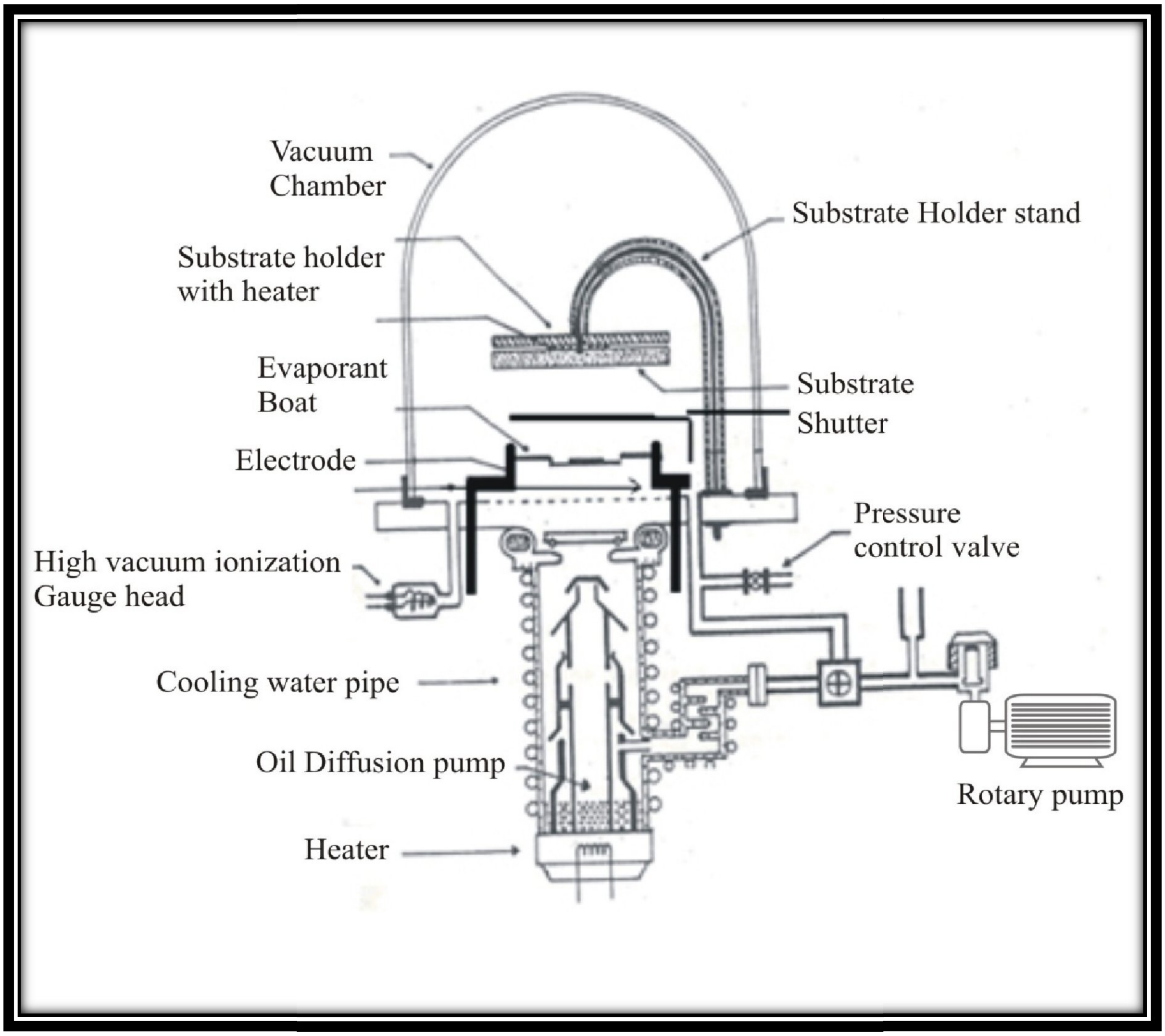


Fig. 3.10 HR Thermal evaporation system

The benefits of HR evaporation system are listed below.

- Easy in operation.
- higher vacuum
- Uniform deposition rate.
- Constant temperature of Substrate
- Deposited films having excellent quality.

Disadvantages of (HR) are as below.

- Low deposition rate.
- It takes lengthy time to attain required temperature and vacuum.
- Contaminations because of evaporation’s source and heaters.
- Level of input power is low.

3.3.5.2.2 The Electron Beam (EB) Evaporation

In this type of technique, extremely pure films can be fabricated. This evaporation allows us to evaporate almost all materials at any rate. The material to be deposited is vaporized in the vessel and formed vapors are in their purest form. More than one source units exist for the deposition of multiple materials. The electrons are released from heated filament which decreases the probability of film contamination.

Fig. 3.11 Crucible of EB system

The electron filament cathode assembly is biased negatively and anode grounded from 4 – 20 kV which accelerate the electrons. A transverse magnetic field is applied which serve to turn aside the electron beam at angle 270^o circular arc and focus the electron beam on the earth and source material. Electron beam evaporates the source material to be deposited on the substrate.

Temperature of substrate, film thickness control, loading and unloading of film, vacuum formation is almost same as it is in HR evaporation system. [11]

3.3.5.2.3 Close-Spaced Sublimation (CSS)

This process is carried out in a close-space at atmospheric pressure, in this process the material is transferred from source to target (substrate) through a gas this method is known close spaced sublimation or close-spaced vapor transport (CSVT)**.**

In this technique the distance between source and substrate is about 1.5mm and both are joined with carbon blocks, infrared heaters are used to heat them and they are held by quartz spacer, the following figure is showing its structure.

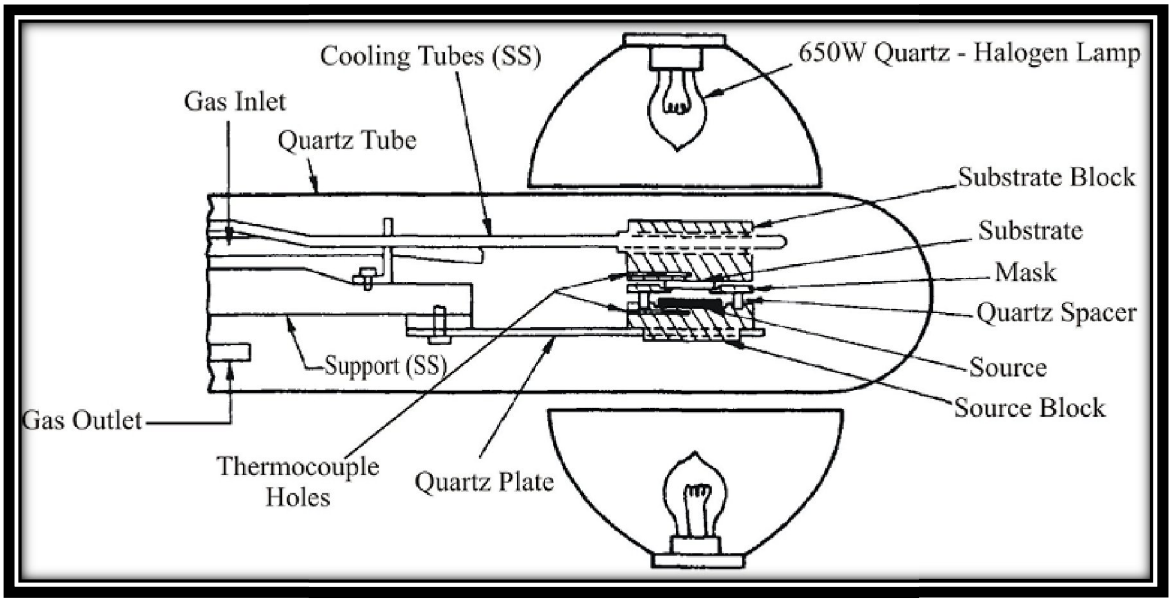


Fig. 3.12 Block Diagram of Close-Spaced Sublimation System

Fig. 3.12 shows the substrate susceptors and source that are made of highly dense purified graphite. Quartz halogen lamps are used to heat graphite blocks and to control their temperature thermocouples are used. Stainless steel tube is used in substrate block which sustains the temperature of the substrate and the spring action of the cooling tube allows good thermal contact between the substrate and the substrate block. Quartz spacer is used as separator between source and substrate which is hold up by quartz plate and this entire arrangement is placed in a quartz tube. Ambient gas and its pressure and source can be controlled independently while in running operation [12].

3.3.5.3 Advantages of the Physical vapor Deposition

Advantages of PVD are listed below.

- The properties of substrate are improved with deposition of film using PVD technique.
- Approximately every variety of inorganic materials can be use while in organic hardly some of materials are appropriate on behalf of this purpose.
- Environmentally friendly technology than a few others such as electroplating.
- With the use of this technique, temperature of substrate can be varied on behalf of a high value.
- The PVD evaporated material adherence is good with substrate.
- Film of polymeric material can also be grown using PVD through certain exemption.

3.3.5.4 Disadvantages of the Physical Vapor Deposition:

Disadvantages of PVD are listed below

- It is a line of sight technique and is very not easy to coat undercuts and alike surface features.
- Higher Equipments and capital cost.
- The Process needed higher quantity of heat, for that reason suitable cooling systems is necessary.
- The rate of coating a film is generally reasonably slow.

3.4 Criteria for the selection of Deposition technique

There are a number of general requirements for several depositing technique to build up a thin film. These are substrate selection, rate of growing, uniform deposition, broad window of processing, adoption of various circumstances of operation, decrease in cost, compactness when various machines are needed, environmental effect and lesser growth rate which allow good control of procedure.

A better film deposition method resolves many practical issues. To choice of suitable deposition method for a specific purpose, the useful points are listed below.

- Degree of cleanliness of a given deposition material.
- How energy is supplied to material to evaporate.
- How to lessen the depositing cost of film.
- How to decrease deposition time of film.
- What are methods to decrease dissolved gases in source material that could be shown in film through the deposition process?
- How should we get ready substrate on behalf of deposition of film?
- How we get consistent thickness of thin film [13].
- Is there fine adherence among substrate plus material for deposition?
- What restrictions are forced by substrate *e.g.* material, size, temperature and stability?
- What is the mandatory deposition rate?
- Films depositing purpose?
- What are safety concerns (toxicity, and operation of system) [5]?

Summary:

In this chapter different designs of OPV and different techniques of film deposition were discussed. OPV devices consist of single layer, bilayer, bulk heterojunction, tandem solar cells etc. Efficiency of single layer is lower than bilayer, the deficiencies in bilayer were removed in bulk heterojunction solar cells, tandem solar cells were introduced to increase the Voc of the device. Similarly CVD and PVD are the two main techniques were described for the film deposition. PVD was selected for film deposition and deposition carried out in heat resistive thermal evaporator using high vacuum.

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Chapter 4

EXPERIMENTAL WORK

4.1 Experimental work

On the basis of previous research of bilayer devices this experimental procedure was adopted. The fabrication process was carried out with physical vapor deposition technique (HR thermal evaporation) under vacuum less then10^6 mbar. During thermal evaporation the materials e.g. CuPc, PCBM, Ag, and Al were evaporated to be deposited on the ITO substrate. This deposition technique produced a uniform layer of these materials. Upon heating the material present in the crucible evaporate and deposit on the substrate, then condense suddenly to produce uniform layer. To get the uniform layer the evaporation rate was kept slow.

The performance of these fabricate devices was monitored by measuring the I-V characteristics, optical performance, and using impedance spectroscopy.

4.2 Materials

CuPc (copper phthalocyanine) was used as an electron donor material and PCBM (Phenyl C_{60} Butyric acid Methyl Ester) was used as acceptor material. After the well research these materials were chosen for this work CuPc and PCBM are the good donor and acceptor materials respectively.

ITO (Indium tin oxide) was used as the front electrode that was coated on the glass substrate, Al was used as the back contact material deposited through thermal deposition using contact mask. The complete device is placed in the glove box filled with nitrogen to avoid degradation.

4.3 Substrate cleaning

Before the fabrication of solar cell the ITO coated glass substrates need to be cleaned. Substrates were etched from both sides using concentrated HCL, centrally protected ITO substrate were placed in to the HCL solution for 5 minutes then ITO from both unprotected sides of substrates were removed. These etched substrates were placed in detergent solution and then sonicated for 10 minutes, and after that substrates were shifted to the deionized (DI) water for 10 minutes, then substrates were placed in to the acetone solution for 10 minutes again being sonicated these substrates were placed in to the IPA (isopropanol acid) solution for 10 minutes.

4.4 Fabrication of Devices

The fabrication process was carried out in HR thermal evaporator as shown in fig. the HR thermal evaporator in Leybold Heraeus (550V A type) high vacuum coating plant, using vacuum of 5×10^{-5}mbar. The plant is present in PCRET Islamabad all the research work has been done there.

Fig. 4.1 HR thermal evaporation plant

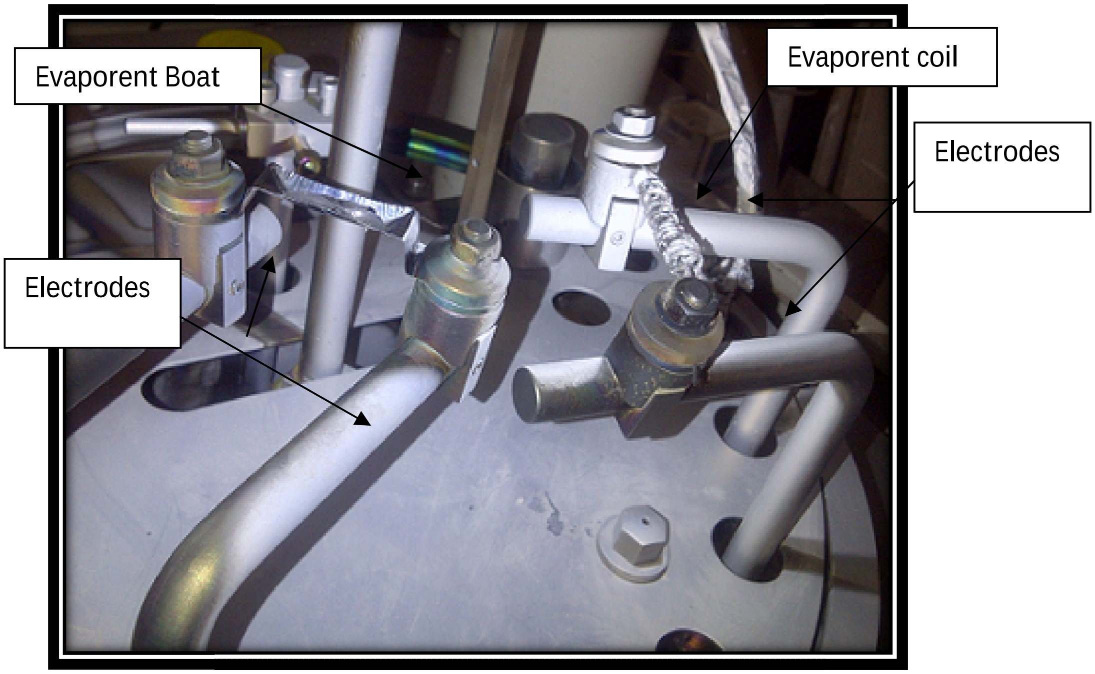

Fig. 4.2 Internal view of HR thermal evaporator vacuum chamber

Before the fabrication of devices the proper vacuum condition is necessary to get better quality of film. Good vacuum is necessary to avoid the contamination like dust and oxidation. It is necessary to cool down the HR plant before unloading the devices or lifting the vacuum chamber to sustain the temperature.

In this work bilayer devices were fabricated as shown in fig. in these devices every material was deposited individually on top of other material. ITO coated substrate were used for each film deposition.

The ITO coated substrates were placed in the vacuum chamber and before the deposition of film the vacuum of 10^{-5} mbar was attained within 30 to 45 minutes. The materials were placed in the bolt where they were heated up to evaporation level. Firstly the layer of donor material CuPc was deposited with the evaporation rate of 1Ấ/s to 2Ấ/s. Intermediate layer of silver Ag was deposited with evaporation rate of 0.3Ấ/s followed by the deposition of acceptor material PCBM with evaporation rate of 1Ấ/s to 2Ấ/s. Al was deposited on the top of these materials as back contact using contact mask with evaporation rate of 5Å/s each with an active area of 0.13cm^2. Total 4 devices were fabricated and tested. The reference device without interlayer was fabricated. The devices that are fabricated in HR thermal evaporation plant are listed below.

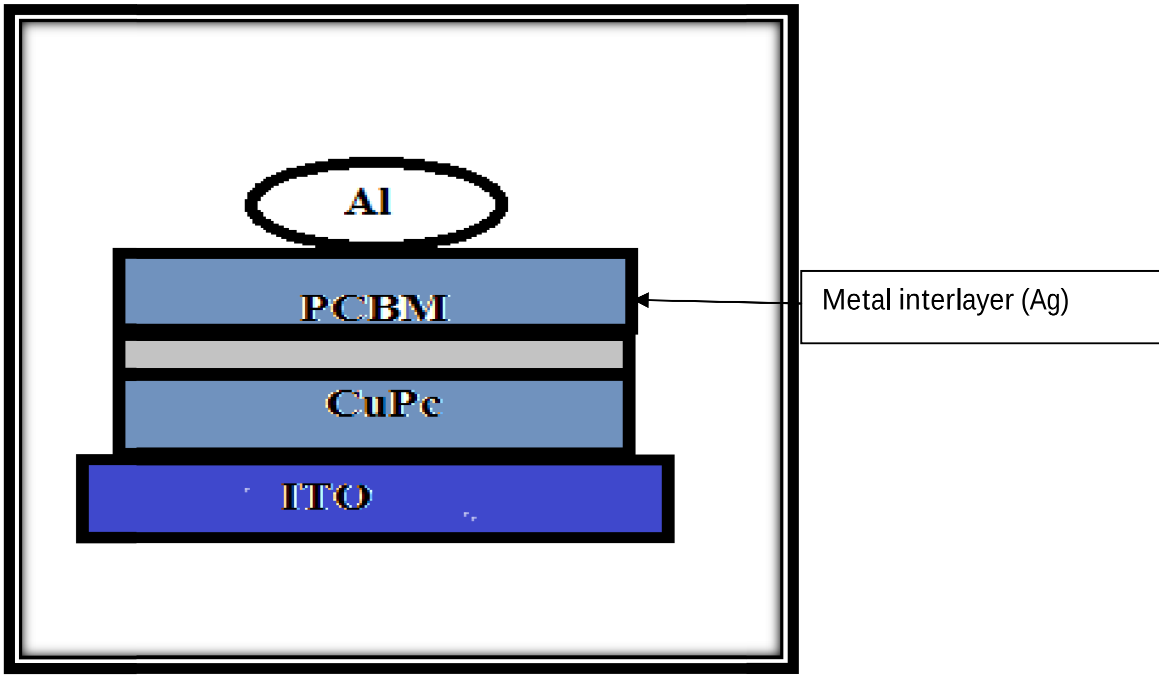

Fig. 4.3 Fabricated stack of different organic deposited on ITO substrate

1. ITO/ CuPc(100nm)/ PCBM(100nm)/ Al
2. ITO/ CuPc(100nm)/ Ag(0.8nm)/ PCBM(100nm)/ Al
3. ITO/ CuPc(200nm)/ Ag(0.3nm)/ PCBM(200nm)/ Al
4. ITO/ CuPc(200nm)/ Ag(0.5nm)/ PCBM(200nm)/ Al

The thickness of each film and the deposition rate was monitored with quartz crystal monitor (QCM).

4.5 I-V characteristics

I-V characteristics of these devices were tested under illuminated condition using keithley sourcemeter; these devices were placed in the glove box under sun simulator with the active layer facing toward the light. The voltage was applied with sourcemeter across device from -0.5V to 0.5V and -5V to 5V the current was measured with these devices in illuminated conditions. Connecting wires were used to connect devices with keithley sourcemeter.

4.6 Optical characterization

Optical properties of the devices e.g. transmittance, absorption and reflection were determined through UV-VIS-NIR spectrometer model LAMDA 950. UV-VIS-NIR is shown in the following fig. With these parameters we can find band gap, refractive index and extinction coefficient. Different spectrum ranges are given below.

- wavelength between 190 to 380nm is ultraviolet region
- wavelength between 380 to 750nm is visible region
- wavelength between 750 to 1100nm is short-wave near infrared region
- wavelength between to 1100 to 2500nm is long-wave near infrared region

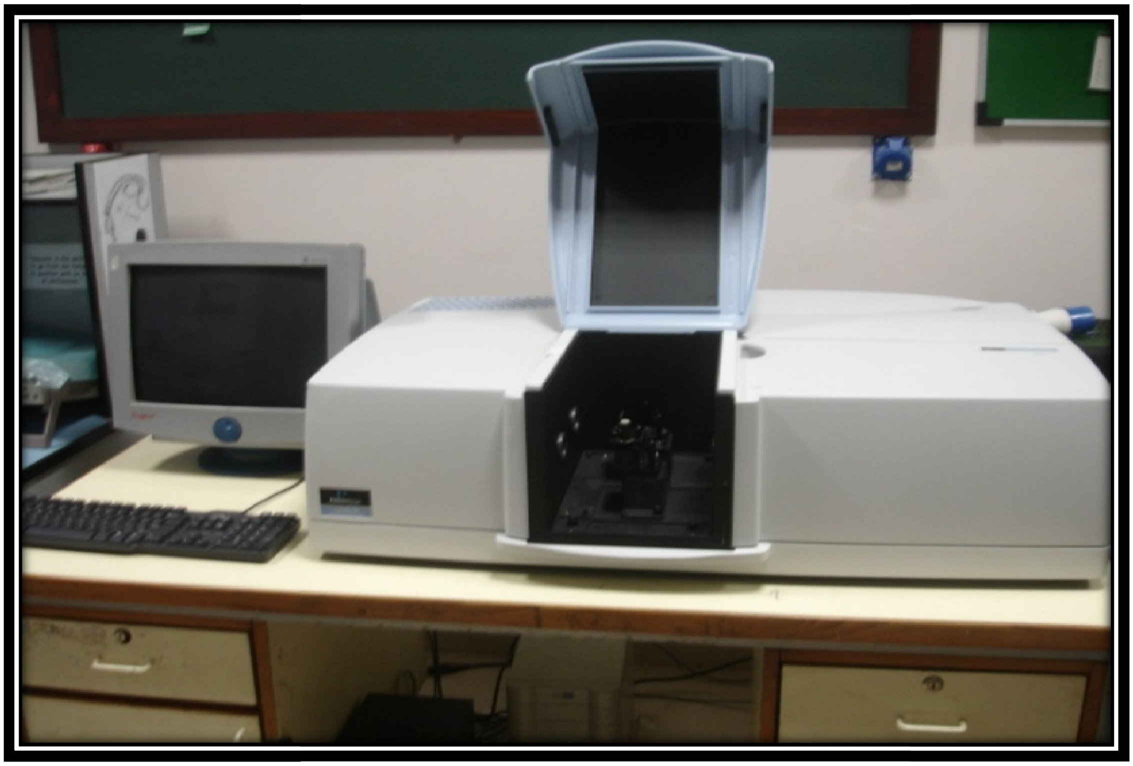

Fig. 4.4 UV-VIS-NIR spectrometer

4.7 Impedance spectroscopy

Impedance spectroscopy was taken using LCR-meter. With this meter 14 parameter can be measured the LCR meter with respect to frequency is shown in the fig. Impedance spectroscopy was taken out to identify the traps in the devices.

Impedance spectroscopy provides frequency resolved information. Which can isolate the contributions of different components regions (e.g. bulk, material/contact and interface between the n and p type regions) to the total electrical properties of heterojunction devices through difference time constants of each element [3, 4, 5].

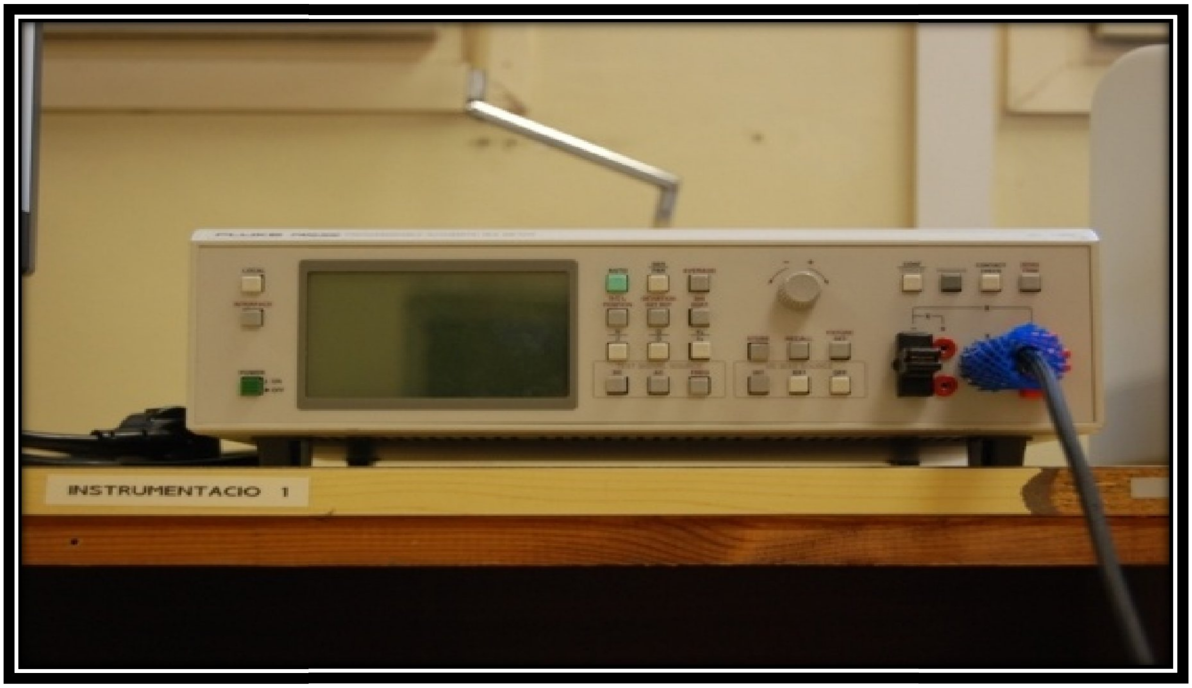

Fig.4.5 LCR meter

Summary

The fabrication process was carried out with physical vapor deposition technique (HR thermal evaporation) under vacuum less then10^{6} mbar. During thermal evaporation the materials e.g. CuPc, PCBM, Ag, and Al were evaporated to be deposited on the ITO substrate. Before the fabrication of solar cell the ITO coated glass substrates were cleaned. After cleaning the substrate donor and acceptor materials were deposited. After the fabrication of these devices these devices were characterized with I-V characteristics, Impedance spectroscopy and optical properties.

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Chapter 5

RESULTS AND DISCUSSION

In this work Devices have been constructed in heat resistive vacuum. Donor and acceptor materials were coated one by one through thermal evaporation on ITO coated slides.

ITO was used as front contact on which CuPc (copper phthalocyanine) was used as excellent electron donor and have a great advantage of carrier mobility and photo properties, heat resistance, light-stability and high optical absorption in the visible range and are applied for solar cells [1]. And then PCBM (Phenyl-C60-Butyric-Acid-Methyl-Ester) was used as acceptor after that Al was used as back contact.

These 4 devices are differentiated by active layer and metal interlayer thicknesses. In this work 1st two devices consisted of with 100nm thickness of donor and acceptor each and differentiated by a thin layer of metal at donor and acceptor interface. After results of these devices we made next two devices with 200nm thickness of donor and acceptor because of low absorption in 1st two devices.

In this work our focus was to increase the Voc of these devices and to characterize the behavior of different devices. In previous work silver metal layer was used to increase Voc in tandem solar cell, Ag was inserted between two cells in dual heterojunction solar cells and their Voc increased as compare to single junction solar cell. And in this work we try metal interlayer at donor/acceptor interface to check the Voc of the device.

In this work the four OPV devices have been constructed their structure is as below.

- ITO/CuPc(100nm)/PCBM(100nm)/Al
- ITO/CuPc(100nm)/Ag(0.8nm)/PCBM(100nm)/Al
- ITO/CuPc(200nm)/Ag(0.3nm)/PCBM(200nm)/Al
- ITO/CuPc(200nm)/Ag(0.5nm)/PCBM(200nm)/Al

The parts of results and discussion to characterize these devices are as following.

- IV characteristics
- Optical properties

5.1 I-V characteristic

IV curves are used to characterize the electrical properties of a solar cell depends on electrodes active regions to benefit carrier injection, charge transport and exciton dissociation etc.

The electrical performance of solar cell is described by its Current-Voltage (I-V) characteristic curve, which is used to determined device and material properties.

Current-voltage characteristics or IV curve is a relationship, typically represented as chart of graph, between the electric current through a circuit, device, or material and the voltage, or potential difference across it.

I-V curve gives the Information about the Voc, Isc, and FF of the device which is sufficient information for a solar cell to characterize the device as solar cell.

In this work we checked device's IV characteristics using keithley source meter, vacuum box, connecting wires and sun simulator. First we placed device in vacuum box under sun simulator and device is connected to source meter through connecting wires, one terminal is connected with ITO and other is with Al contact. Voltage applied through source meter and Light through sun simulator to excite electrons, device's current noted to plot IV curve.

First two devices IV characterization is given below.

- ITO/CuPc(100nm)/PCBM(100nm)/Al
- ITO/CuPc(100nm)/Ag(0.8nm)/PCBM(100nm)/Al

These two devices are with 100nm thickness of donor and acceptor, In1st device CuPc was thermally deposited as donor on ITO coated slide then PCBM (acceptor) was deposited through thermal deposition and at the end Al was used as back contact material deposited through thermal deposition as well. In second device Ag was inserted between CuPc (donor) and PCBM (acceptor) interface using the same thermal deposition technique, in previous researches Ag was used between two cells in tandem cells structure to increase the Voc of the device, Ag interlayer is usually used to increase Voc of the device, it increased absorption within the thin organic film. And in this work we checked device behavior by placing Ag at donor and acceptor Interface. After getting IV results of these two devices we compare both device's Voc and Isc.

IV graphs of both devices are shown in the following Fig. 5.1.

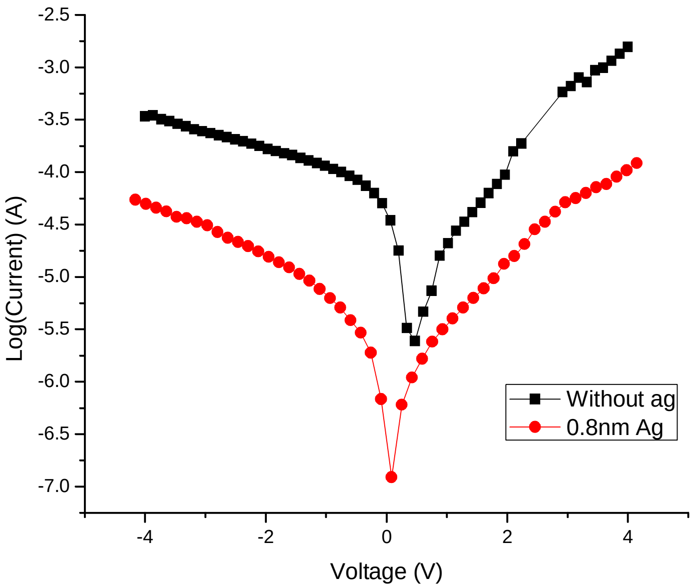


Fig. 5.1 V-I graph b/w without Ag & 0.8nm

It can be seen from the I-V curve as presented in Fig 5.1 it shows the I-V curve of two devices 1st is reference device without interlayer of silver with 100nm thickness of donor and acceptor each and 2nd is with 0.8nm of Ag interlayer at donor (100nm) and acceptor (100nm) interface.

The following table is showing the different parameters of organic solar cells.

Table 5.1

Sr#	Device	Voc	Isc
1	Without Ag	0.455 V	0.0000415 A
2	0.8nm Ag	0.085 V	0.000000123 A

Table 5.1 shows that the Voc and Isc decreased from 0.455V to 0.085V and 0.0000415A to 0.000000123A respectively. As silver is added at the interface of donor and acceptor due to limitation of the metallic intermediate layer that is the diffusion of metal into the organic layer during thermal evaporation [2, 3, 4]. Diffusion leads to small shunt resistance to reduce the Voc and Isc of the device. The metal atoms diffused in to active layer and forms charge traps. When silver is added it takes charges and creates traps at interfacing point which recombine electrons and holes hence Voc, Isc, FF, and its efficiency decreased.

In this work we recorded absorbance data of these devices which shows low absorbance of devices that's why we increased donor/acceptor thickness and modify the silver thickness as well.

Next two devices structure described below.

- ITO/CuPc(200nm)/Ag(0.3nm)/PCBM(200nm)
- ITO/CuPc(200nm)/Ag(0.5nm)/PCBM(200nm)

These devises has double donor and accepter thicknesses with modified thicknesses of silver. IV data of these devices noted and graphs are shown in Fig. 5.2.

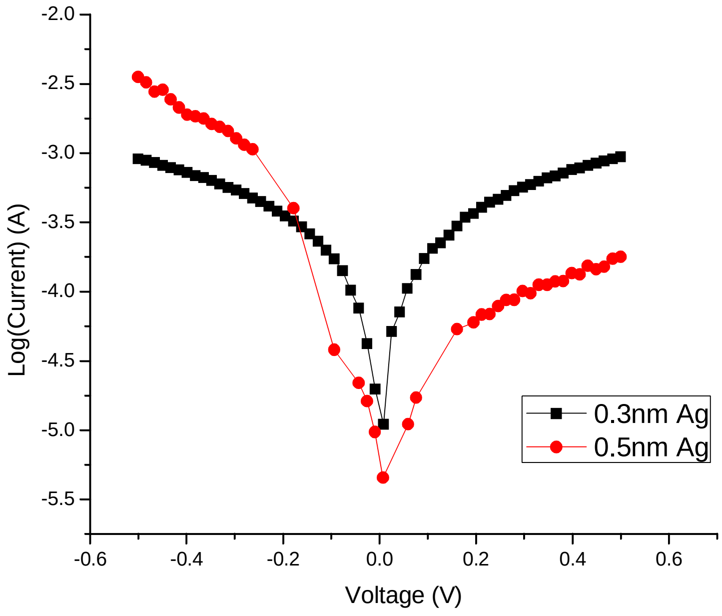


Fig. 5.2 V-I graph b/w 0.3nm & 0.5nm

Fig. 5.2 shows I-V characteristics of 2nd two devices in which donor (200nm) and acceptor (200nm) with silver interlayer thickness of 0.3nm and 0.5nm respectively.

The following table is showing the different parameters of these OPV devices.

Table 4.2

Sr#	**Device**	**Voc**	**Isc**
1	0.3nm Ag	8.52×10^{-3} V	1.09×10^{-5} A
2	0.5nm Ag	2.53×10^{-3} V	6.25×10^{-6} A

Table 5.2 shows that as the amount of silver increased Voc and Isc of devices decreased from 8.52×10^{-3}V to 2.53×10^{-3}V and 1.09×10^{-5}A to 6.25×10^{-6}A respectively this is because of silver addition, it was noted that as the amount of silver increased more traps created and more recombination occurs. Different parameters of OPV devices are showing the same effect as it was noted in 1st two devices that as the thickness of silver increases in devices traps increases their Voc, Isc, FF and efficiency decreased.

IV results showed that traps created in OPV devices to identify these traps Impedance spectroscopy carried out. Results of impedance spectroscopy defined the traps created in OPV devices.

5.2 Impedance Spectroscopy

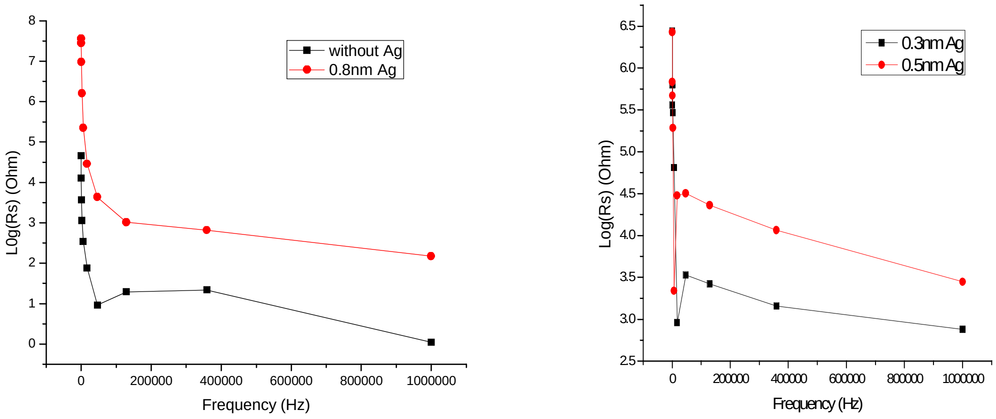
Impedance spectroscopy provides frequency resolved information. Which can isolate the contributions of different components regions (e.g. bulk, material/contact and interface between the n and p type regions) to the total electrical properties of heterojunction devices through difference time constants of each element [5, 6, 7].

5.2.1 Series Resistance

Series resistance (Rs) of these devices is due to bulk and contact resistance [8, 9]. Series resistance of OPV devices are shown in the Fig 5.3 IS data was recorded with LCR testmeter, LCR testmeter was connected with devices through connecting wires with ITO and Al contacts.

Fig. 5.3 (a) shows series resistance of 1st two devices (without Ag and with 0.8nm Ag) with 100nm thickness of donor and acceptor and Fig 5.3 (b) shows series resistance of 2nd two devices (0.3nm and 0.5nm) with 200nm thickness of donor and acceptor.

Fig. 5.3 (a) shows that series resistance of without silver device is low as compare to 0.8nm Ag interlayer device which indicates that when silver added to the device their bulk and contact resistance increased. Increase in series resistance of device is one of the reasons to decrease in Voc and Isc of the device shown in Table 5.1 and Table 5.2 Fig. 5.1 and Fig. 5.3 (a) shows that when Rs is low Voc and Isc is high and when Rs is high Voc and Isc decreased. Fig. 5.3 (b) shows the same effect that as the thickness of Ag increased at donor acceptor interface Rs increased and Voc and Isc decreased.



(a) (b)

Fig. 5.3 Series resistance (Rs) of OPV devices with changing frequency

Fig. 5.4 shows the combine result of all devices that as the amount of Ag increases their Rs increases and as the amount of Rs increases the Voc and Isc decreased as shown in Fig. 5.1 and 5.2.

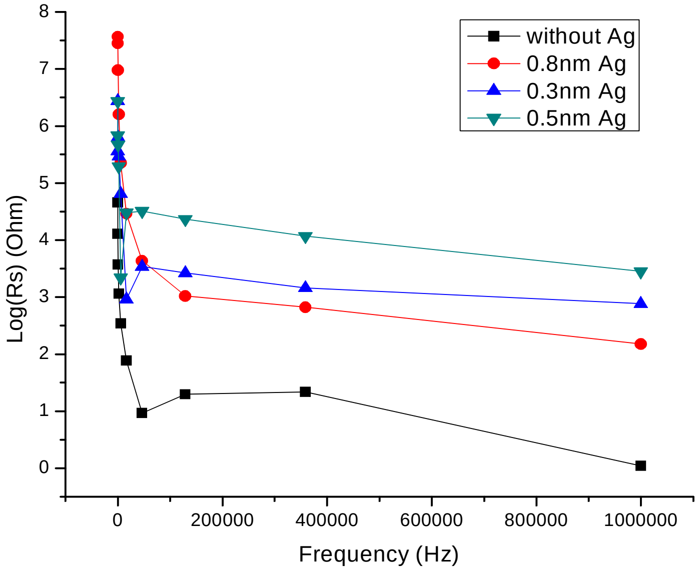


Fig. 5.4 Series resistance of all OPV devices

5.2.2 Parallel Resistance

Parallel resistance (Rp) of OPV devices also describes the electrical behavior of these devices. Parallel resistance gives the information about traps generated in OPV devices.

Fig. 5.5 shows the parallel resistance of OPV devices, parallel resistance Rp is due to recombination in the depletion region [10, 11, 12]. Fig. 5.5 shows that at low frequency the Rp decreases as the amount of Ag increases because traps responds on low frequencies [13] the slight decrease in Rp is due to the leakage paths which can physically due to generation-recombination current within the depletion region [14] and as the amount of Ag increases traps increases as a result Rp decreases and then Voc, and Isc decreased shown in Fig. 5.1 & 5.2.

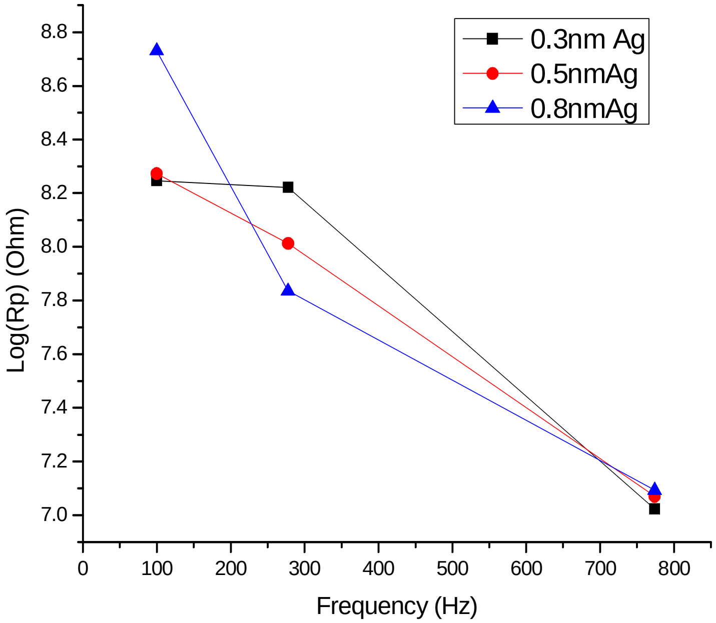


Fig.5.5 parallel resistance of OPV devices with Ag

5.2.3 Impedance

Electrical impedance is the measure of the resistance that a circuit presents to current when voltage is applied. Quantitatively, it is the complex ratio of the voltage to the current in an alternating current (AC) circuit. Impedance extends the concept of resistance to AC circuits, and possesses both magnitude and phase, not like resistance, which has only magnitude. When a circuit is determined with direct current (DC), there is no difference between impedance and resistance. In this work voltage applied to these devices and magnitude of Impedance data that we collected is shown in the Fig. 5.6, 5.7 and 5.8.

Fig. 5.6 shows that as the amount of Ag added to the interface of donor and acceptor its impedance increases and its Voc and Isc decreased shown in Fig. 5.1.

This is because traps increases as impedance graphs showing that impedance increases due to increment of Ag at interfacing point, high impedance is indicating more traps in the device.

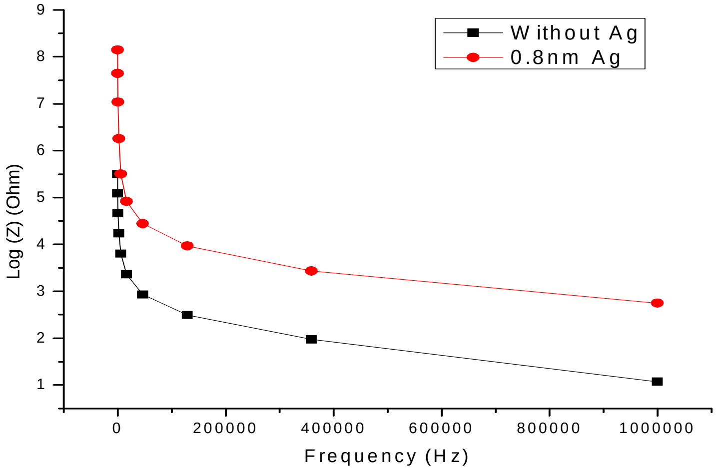


Fig. 5.6 Impedance of 1st two OPV devices

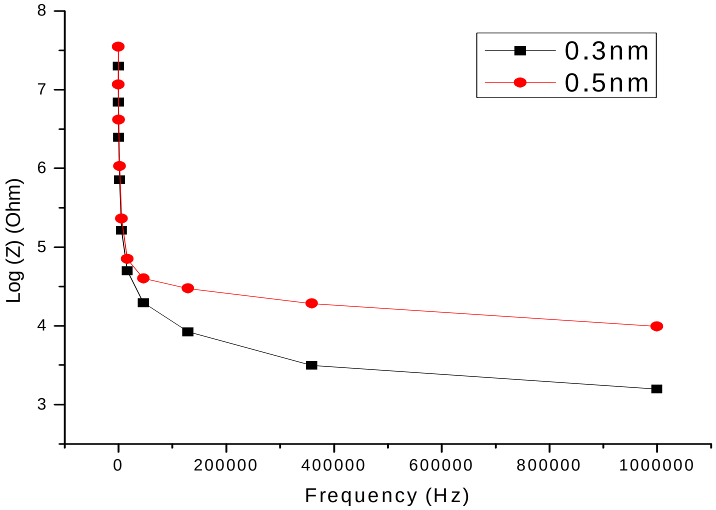


Fig. 5.7 Impedance of 2nd two devices

Fig. 5.7 shows the same effect as the amount of Ag increases its Impedance increased and Voc and Isc decreased, 0.5nm Ag device has higher Impedance and Lower Voc and

Isc. High amount of Ag device (0.5nm) has more traps as shown in impedance spectrum of device it has higher impedance than low amount of Ag device (0.3nm).

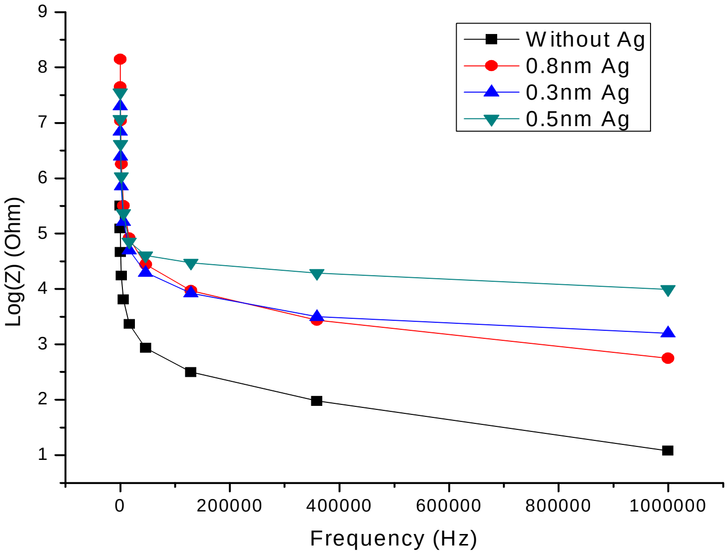


Fig.5.8 Impedance of all OPV devices

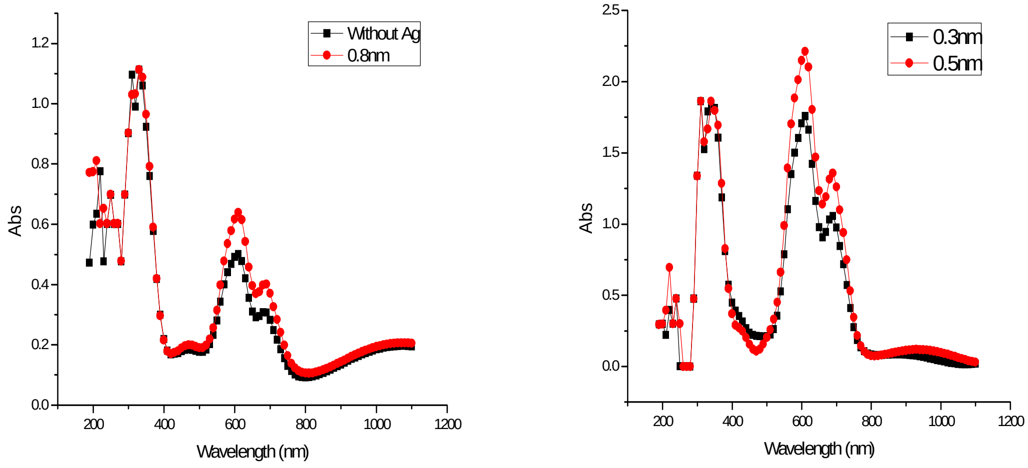
Fig. 5.8 shows the all devices combine Impedance effects here we can see that as Ag thickness increases the device's impedance increased and their Voc and Isc decreased. High amount of Ag has high Impedance due to more traps.

5.3 Optical Properties

Solar cells are built from different elements, and beside their electric importance most of them also have to fulfill important optical requirements. The number of photons can be absorbed by solar cell is determined by the optical properties of the device, which in turn , is the property of the material used to absorb light and the geometry in which it is used.

Solar cell light absorption is the optical parameter called the absorptivity that is most useful when assessing potential absorber material for solar cells. The quantum absorptivity is the fraction of the incoming light at given photon energy to absorb by the material to produce an excited state such as an electron hole pair [15].

Fig 5.9 (a) shows change in the absorbance spectrum as amount of silver is added its absorbance increases but Voc and Isc decreases unexpectedly because of traps generation and recombination.



(a) (b)

Fig. 5.9 Absorbance spectrum of OPV devices

Figure 5.9 (b) shows high increase in absorbance due to increase in donor and acceptor thicknesses, and the higher amount of silver device has higher absorbance but unexpectedly low Voc and Isc due to more recombination as amount of silver increases.

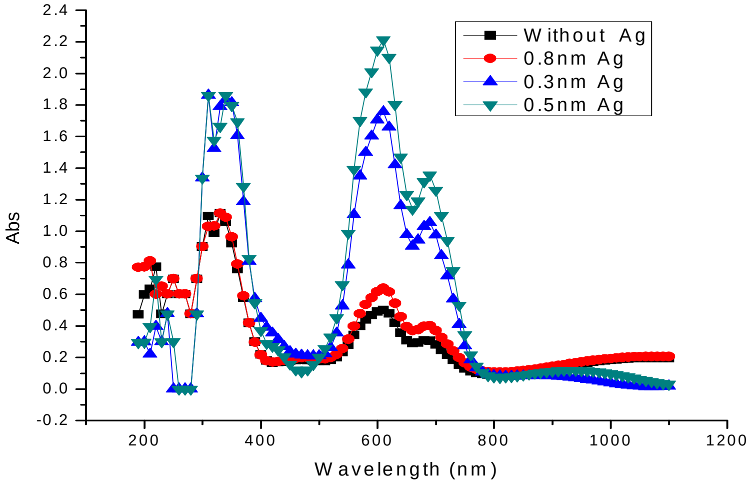


Fig. 5.10 Absorbance spectrum of OPV devices

Fig.5.10 shows the absorbance spectrum of all devices which is showing that as Ag is added to the reference device its absorbance increases, then thickness of donor and acceptor increases to increase the absorbance, high absorbance spectrum from 400 to 700nm is observed, 0.5nm Ag interlayer device has high absorbance than 0.3nm Ag interlayer device.

We were expecting increase in Voc and Isc from absorbance spectrum but due to creation of traps Voc and Isc decreased as recombination increases.

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Summary

In this chapter devices characterization was carried out using different parameters. It was observed that Voc and Isc decreased from the reference device as we add metal layer between donor/ acceptor. To find the reason of decrease in Voc and Isc we perform Impedance spectroscopy and series parallel spectrum, these spectrums shows that upon the addition of silver traps generated in the device these traps capture the incoming electron and as result these traps decrease the Voc, Isc, FF, and efficiency as well. And optical data was taken to check the absorbance and transmittance of all devices.

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Conclusion and Recommendations

Conclusion

New approach was adopted in this work that was the introduction of metal interlayer at donor/ acceptor interface to increase Voc and Isc. It was noted that Voc and Isc of the device was decreased then the reference device (without metal inter layer).

It was found that metal layer takes charge from the donor acceptor interface and produced charge traps in which electrons were recombined and hence the Voc and Isc of the device was reduced.

To verify these traps we perform Impedance spectroscopy, taking series resistance (Rs), parallel resistance (Rp), and impedance spectrum with changing frequencies.

Then absorbance data suggested that devices thickness should increased to increase the photon absorbance then we tried to resolve these issues by changing the thicknesses of active region and metal interlayer as well, but as the amount of Ag was increased more traps were produced and more decrease in Voc and Isc occurred.

Recommendations

The system is best in all term as a lab solar cell fabrication but can be more beneficial if some changes will be done like.

- The process of cleaning should be carried out under full concentration.
- The deposition process should be take place in latest HR vacuum thermal evaporator.
- The cells should be annealed
- All 14 parameters taken from LCR meter should be consider for better characterization of solar cell.
- Wires should be connected carefully to make it sure that contact should be save.
- Cells should be placed in vacuum box for long duration.

Annexure I

Fabrication and Characterization of CuPc and PCBM based organic Solar cell with metal Interlayer

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1. Abstract:

Organic solar cells have potential as an alternative to conventional inorganic solar cell due to low processing cost, flexibility and easy fabrication technique.

The goal of this paper is to study the characteristics of the CuPc and PCBM based organic solar cell by introducing a thin layer of Ag at the interface of donor (CuPc) and Acceptor (PCBM), their photovoltaic and optical properties were investigated. The heterojunction solar cells with silver inter layer and without silver were fabricated through thermal deposition in HR vacuum. The OPV solar cells were characterized using current-voltage graphs, absorbance spectrum and Impedance spectroscopy. Impedance spectroscopy was taken to identify these traps using series resistance, parallel resistance, and Impedance spectrums under different frequencies and optical behaviors of these devices have been investigated with absorbance spectrum.

Introducing Ag to interfacing point decreased Voc, Isc, FF, and efficiency due to generation of charge traps by Silver. The effect of donor/ acceptor and silver interlayer thicknesses was also studied

Keywords. HR thermal evaporator, I-V characteristics, Impedance spectroscopy, Optical properties

2. Introduction:

Organic Photovoltaic (OPV) solar cells are emerging as a third generation of photovoltaic technology. The OPV provides assurance of a low cost solar photovoltaic solution and attracts important academic and industry research. These OPV solar cells have number of benefits over inorganic solar cells. Organic materials are rich to form a solid base for material innovation, the OPV materials have much higher absorption coefficients than silicon, Low energy processing, non-toxic and environmental friendly. The OPV cells have been a focus of research more than last 25 to 30 years [1,2]. In spite of efforts, the device performance is still far from that required for practical application. The limiting factor for the performance is primarily the small exciton diffusion length as compared with the optical absorption. That is why the width of active charge separation and collection region is small. This results in reduction in cell efficiency.

Different techniques have been used to overcome these issues like short diffusion length, width of active region etc. Including use of intercalated conjugated polymer blends [2], charge separation interface, use of high exciton diffusion length materials [3], with alternative geometries of cell e.g. a cell having mixed region of codeposited pigments inserted between the donor acceptor layer [4], and staked tandem solar cell [5]. In tandem solar sell two heterojunctions are deposited. These are separated by a metal layer. The technology has advanced in different device structures including donor/ acceptor heterojunction, tandem structures, and the use of electrically doped transparent layers. The efficiency of all devices could increase from improved understanding of the physics of exciton separation at the donor – acceptor interface.

In this work new approach is adopted in which donor (CuPc) and acceptor (PCBM) were deposited one by one and separated by a thin Ag metal layer. CuPc has high optical, light stability, chemical stability and photovoltaic property. Therefore CuPc was used as a donor material in organic solar cells [16]. Unfortunately, it was found that metal layer takes charge from the donor acceptor interface and produced traps which recombine the electrons and hence reduced the Voc and Isc of the device. To verify these traps we perform Impedance spectroscopy, using series resistance (Rs), parallel resistance (Rp), and impedance spectrum with changing frequencies.

3. Experimental Procedure:

In this work four photovoltaic (PV) cells were fabricated on indium-tin-oxide (ITO) coated glass substrates. The substrates were cleaned using the following process.

ITO coated slides were etched from corners with HCL. Then substrates were placed in to DI water for 10 minutes. After DI water substrates were washed with detergent for 5 minute. Further cleaning was carried out with IPA and acetone in an ultrasonic bath.

These cleaned ITO coated slides were loaded in heat resistive evaporation system, organic layers were vacuum deposited on the clean ITO substrate at base pressure 5×10^{-6} mbar using deposition rate of 5Å/s. Deposition thickness were monitored by a quartz crystal microbalance during film deposition. The deposition order of layers used in OPV devices started with donor (CuPc) layer followed by Acceptor (PCBM) layer and between donor and acceptor metal layer was deposited, then Al wire was evaporated on back side of substrate to obtain ohmic contact through a mask. Four cells were made three with different thicknesses of Ag metal interlayer and one without Ag metal interlayer, cell structure is shown in the Fig. 1.

These prepared structures shown in fig 1 (a) and (b) were characterized by I-V measurements under illuminated conditions in terms of electrical properties using keithley source meter, glove box, connecting wires and sun simulator. Voltage was applied with source meter and Light with sun simulator, device's current noted on a specified voltage values and then I-V curve was plotted.

4. Results & Discussions:

The OPV devices ITO/CuPc/PCBM/Al and ITO/CuPc/Ag/PCBM/Al were characterized in terms of different thicknesses to study their properties and behavior under illuminated condition.

4.1. Current-voltage characteristics:

The electrical performance of solar cell is described by its Current-Voltage (I-V) characteristic curve, which is used to determine device and material properties, electrical properties of a solar cell depends on electrodes active regions to benefit carrier injection, charge transport and exciton dissociation etc.

First two devices structure is given below.

- ITO/CuPc(100nm)/PCBM(100nm)/Al
- ITO/CuPc(100nm)/Ag(0.8nm)/PCBM(100nm)/Al

These two devices are with 100nm thickness of donor and acceptor, In1st device CuPc was deposited as donor on a cleaned ITO coated slide then PCBM (acceptor) was deposited and at the end Al was deposited using contact mask as back contact of substrate. In second device Ag was introduced between CuPc (donor) and PCBM (acceptor) interface using the same thermal deposition technique, in previous researches Ag was used between two cells in tandem cells structure to increase the Voc of the device, it increased absorption within the thin organic film [8]. And in this work we checked device behavior by introducing Ag at donor and acceptor Interface. The semi log plots of I-V data of devices under illuminated conditions are shown in fig 2. Both device's Voc and Isc compared in Fig. 2 and table 1.

Devices 1 is reference device without interlayer of silver with 100nm thickness of donor and acceptor each and device 2 is with 0.8nm of Ag interlayer at donor (100nm) and acceptor (100nm) interface.

Table 1 shows the different parameters of these OPV devices.

The results show that Voc and Isc decreased from 455mV to 85mV and 41.5µA to 0.123µA respectively due to silver introduction at donor/ acceptor interface. Metallic intermediate layer diffused into the organic layer during thermal evaporation [6, 7, 8]. Diffusion leads to small shunt resistance to reduce the Voc and Isc of the device. The metal atoms diffused in to active layer and forms charge traps. When silver is added it takes charges and creates traps at interfacing point which recombine electrons and holes hence Voc and Isc decreased.

The absorbance data of these devices are shown in fig.10 and 11 exhibits low absorbance. So we increased donor/acceptor thickness and modify the silver thickness as well as described below.

- ITO/CuPc(200nm)/Ag(0.3nm)/PCBM(200nm)
- ITO/CuPc(200nm)/Ag(0.5nm)/PCBM(200nm)

These devises were fabricated with double donor and accepter thicknesses and with modified thicknesses of silver. The semi log plots of I-V data of devices under illuminated conditions are shown in fig 3. Both device's Voc and Isc compared in Fig. 3 and table 2.

Fig. 3 shows I-V characteristics of 2nd two devices in which donor (200nm) and acceptor (200nm) with silver interlayer thickness of 0.3nm and 0.5nm respectively.

Table shows that as the amount of silver increased Voc and Isc decreased from 8.52*10^-3V to 2.53*10^-3V and 1.09*10^-5A to 6.25*10^-6 respectively this is because of silver addition, it was noted that as the amount of silver increased more traps created and more recombination occurs. Different parameters of OPV devices are showing the same effect in table 2 as it was noted in table 1 of 1st two devices that as the thickness of silver increased in devices traps increased and their Voc, Isc, FF and efficiency decreased.

I-V results concluded that traps created in OPV devices, to identify these traps Impedance spectroscopy was carried out. Results of impedance spectroscopy defined that traps were created in OPV devices.

4.2. Impedance Spectroscopy:

Impedance spectroscopy provides frequency resolved information. Which can separate the contributions of different components regions (e.g. bulk, material/contact and interface between the n and p type regions) to the total electrical properties of heterojunction devices [9, 10, 11].Series resistance (Rs) of these devices is due to bulk and contact resistance [1,3]. Series resistance of OPV devices are shown in the fig. 4. IS data was recorded with LCR testmeter, LCR testmeter was connected with devices through connecting wires with ITO and Al contacts.

Fig. 4 shows series resistance of 1st two devices (without Ag and with 0.8nm Ag) with 100nm thicknesses of donor and acceptor and of 2nd two devices (0.3nmAg and 0.5nmAg) with 200nm thickness of donor and acceptor.

Fig. 4 shows the series resistance of all devices in 1st devices (without Ag) introduction of 0.8nm silver increased its series resistance and hence Voc and Isc decreased and in 3rd and 4th devices with 0.3nm Ag and 0.5nm Ag respectively have higher series resistance due to higher amount of Ag. As the thickness of silver was increased charge traps increased their Rs increased and as Rs increased the amount of Voc and Isc decreased as shown in fig.4.

Parallel resistance (Rp) of OPV devices also describes the electrical behavior of these devices. Parallel resistance gives the information about traps generated in OPV devices.

Fig. 5 shows the parallel resistance of OPV devices, parallel resistance Rp is due to recombination in the depletion region [9, 11, 12]. Traps responds on low frequencies [13] Fig. 6 shows that at low frequency the Rp decreased as the amount of Ag increased, the slight decrease in Rp is due to the leakage paths which can physically due to generation-recombination current within the depletion region [14]. As the amount of Ag increased traps were increased, as result Rp decreased was observed that was the reason of reduction in Voc, and Isc.

Electrical impedance is the measure of the resistance that a circuit presents to current when voltage is applied. Quantitatively, it is the complex ratio of the voltage to the current in an alternating current (AC) circuit. Impedance extends the concept of resistance to AC circuits, and possessed both magnitude and phase, not like resistance, which has only magnitude. When a circuit is determined with direct current (DC), there is no difference between impedance and resistance. In this work DC voltage was applied to these devices and Impedance data was collected which shows only magnitude with zero phase angles, so this Impedance is same as resistance.

Fig. 6 shows the all devices combine Impedance effects here we can see that as Ag thickness of 0.8nm was introduced to the 1st device it generates charge traps there and hence its Impedance increased. In other 2 devices higher thickness layer has higher Impedance which indicates more traps in the device and decreased Voc and Isc.

4.3. Optical Properties:

Solar cells are built from different elements, and beside their electric importance most of them also have to fulfill important optical requirements. The number of photons can be absorbed by solar cell is determined by the optical properties of the device, which in turn, is the property of the material used to absorb light and the geometry in which it is used.

Solar cell light absorption is the optical parameter called the absorptivity that is most useful when assessing potential absorber material for solar cells. The quantum absorptivity is the fraction of the incoming light at given photon energy to absorb by the material to produce an excited state such as an electron hole pair [15].

Fig. 7 (a) shows change in the absorbance spectrum as amount of silver is added its absorbance increased, more photons were generated but Voc and Isc decreased unexpectedly because of traps generation and recombination. Fig. 7 (b) shows high increase in absorbance due to increase in donor and acceptor thicknesses, the higher amount of silver device has higher absorbance but unexpectedly low Voc and Isc due to more recombination as amount of silver was increased.

Fig. 11 shows the absorbance spectrum of all devices which is showing that as Ag is added to the reference device its absorbance increased, then thickness of donor and acceptor were increased to increase the absorbance, high absorbance spectrum from 400 to 750nm was observed, 0.5nm Ag interlayer device has high absorbance than 0.3nm Ag interlayer device.

We were expecting increase in Voc and Isc from absorbance spectrum but due to creation of charge traps Voc and Isc decreased as recombination increased.

5. Conclusion:

New approach was adopted in this work that was the introduction of metal interlayer at donor/ acceptor interface to increase Voc and Isc. It was noted that Voc and Isc of the device was decreased then the reference device (without metal inter layer).

It was found that metal layer takes charge from the donor acceptor interface and produced charge traps in which electrons were recombined and hence the Voc and Isc of the device was reduced.

Then absorbance data suggested that devices thickness should increased to increase the photon absorbance then we tried to resolve these issues by changing the thicknesses of active region and metal interlayer as well, but as the amount of Ag was increased more traps were produced and more decrease in Voc and Isc occurred.

To verify these traps we perform Impedance spectroscopy, taking series resistance (Rs), parallel resistance (Rp), and impedance spectrum with changing frequencies

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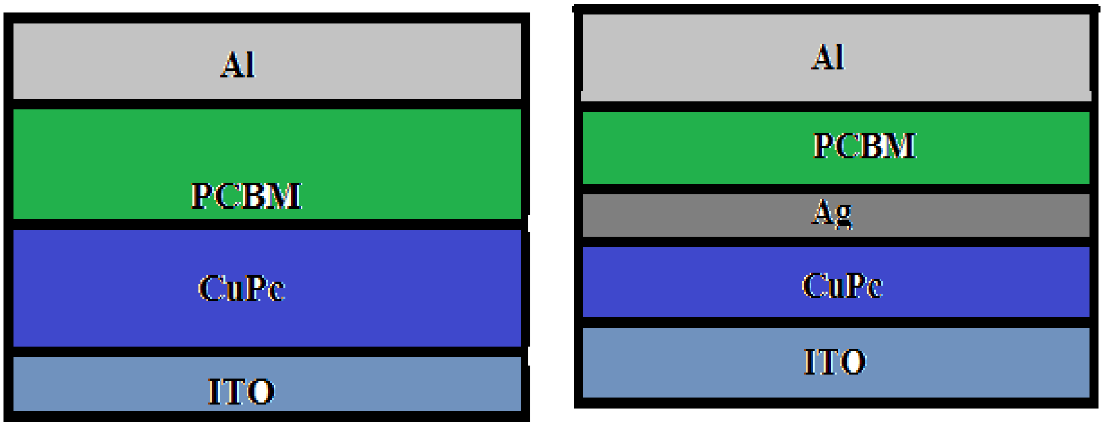


(a) (b)

Fig.1 Substrates structure of OPV cell (a) without silver interlayer & (b) with silver interlayer

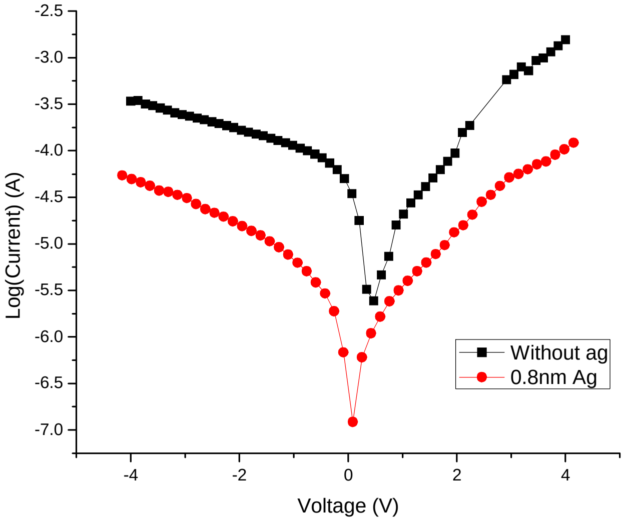


Fig.2. I-V graph b/w without Ag & 0.8nm

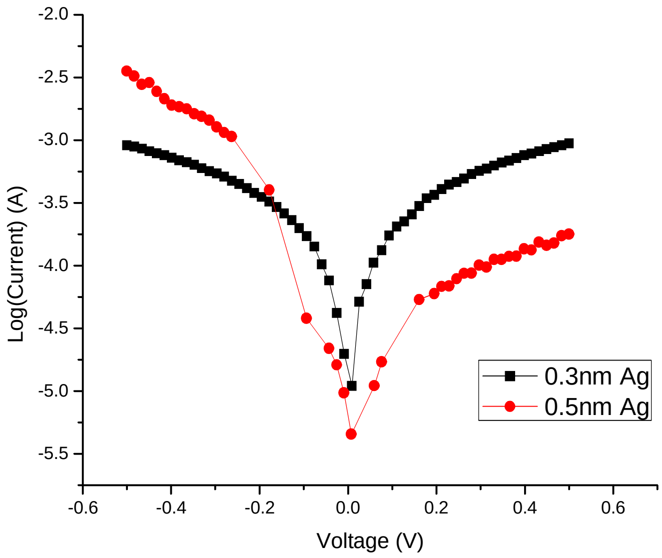


Fig. 3. V-I graph b/w 0.3nm & 0.5nm

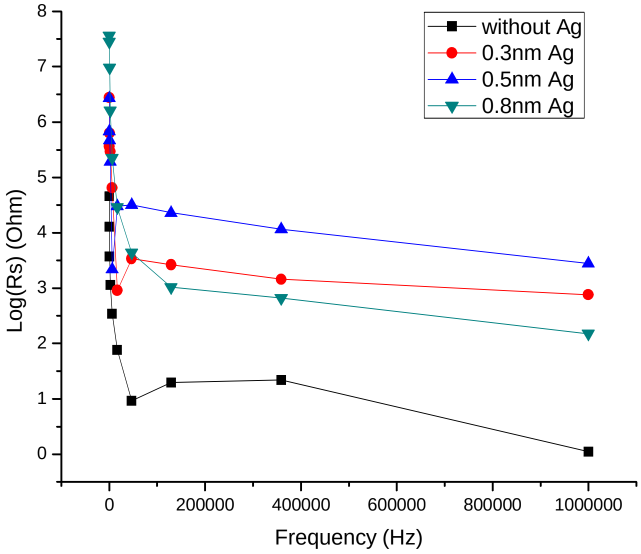


Fig. 4 Series resistance of all OPV devices

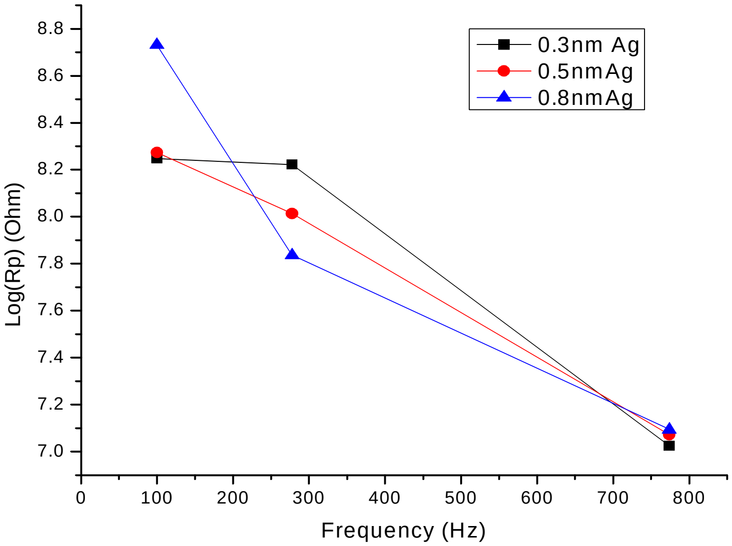


Fig. 5 Parallel resistance of OPV devices with Ag

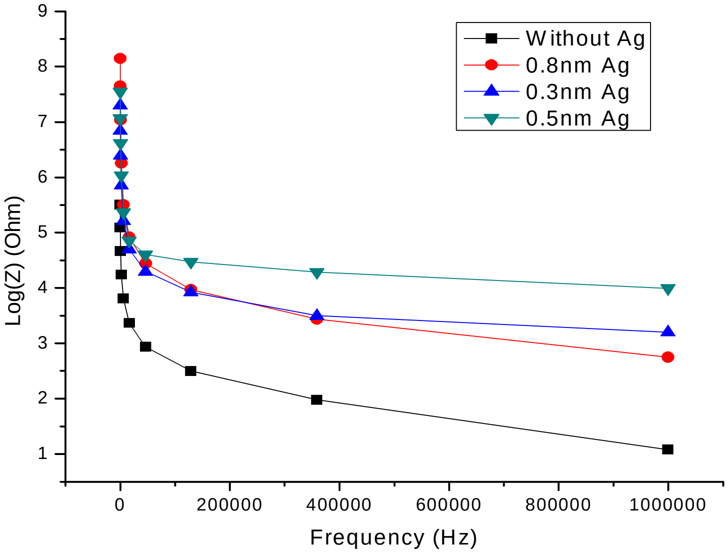
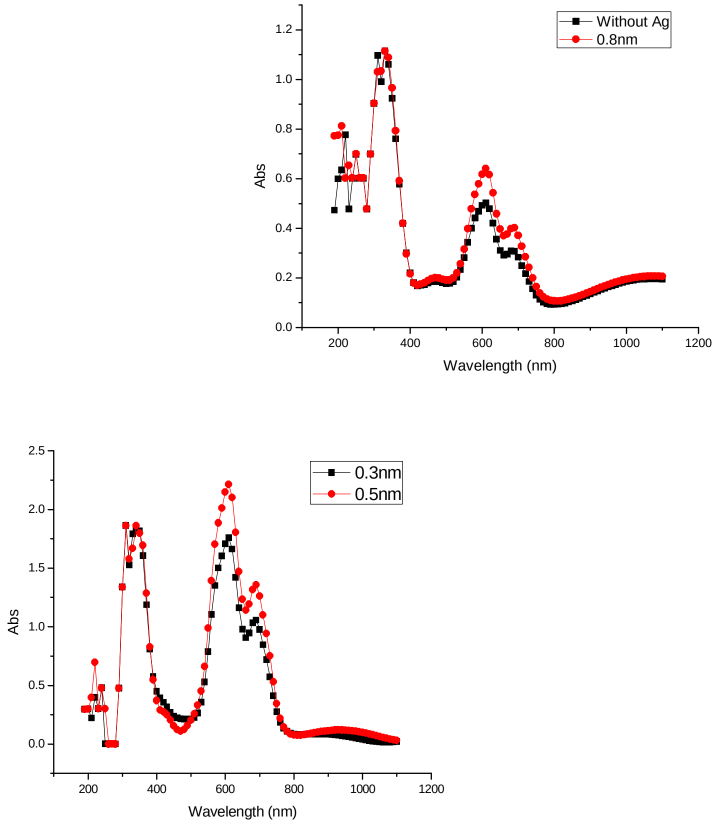


Fig. 6 Impedance of all OPV devices



(a)

(b)

Fig. 7 Absorbance spectrum of OPV devices

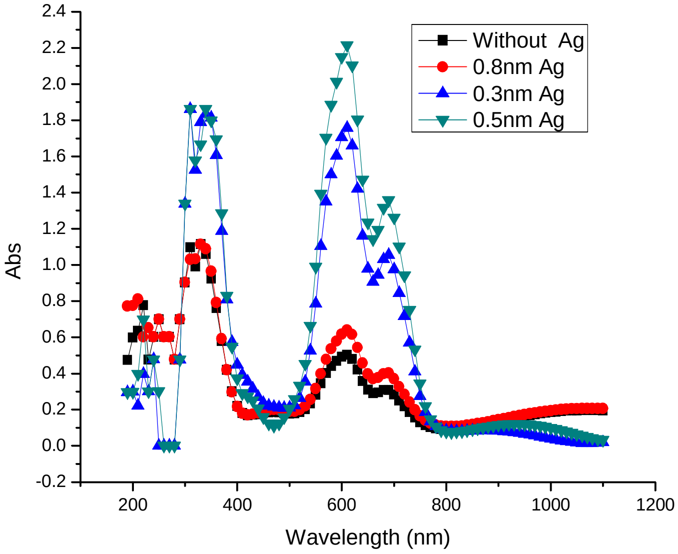


Fig. 8 Absorbance spectrum of OPV devices

Table 1 Comparison of Voc & Isc for 100nm thickness of each.

Sr#	**Device**	**Voc**	**Isc**
1	Without Ag	0.455 V	0.0000415 A
2	0.8nm Ag	0.085 V	0.000000123 A

Table 2 comparison of Voc and Isc for 200nm thickness of each

Sr#	**Device**	**Voc**	**Isc**
1	0.3nm Ag	8.52×10^{-3} V	1.09×10^{-5} A
2	0.5nm Ag	2.53×10^{-3} ?	6.25×10^{-6} A

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Annexure-I