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作品名稱 **FABRICATION AND
CHARACTERIZATION OF CARBON
NANOTUBE DOPED PHOTOVOLTAIC
CELLS**

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ABSTRACT

Nowadays, the increase in population and the rapid depletion of nonrenewable energy sources brings the need for energy. In this case, scientists are forced to develop technologies by using renewable energy sources. Sun is the unlimited and renewable energy source.

Organic solar cells absorb the light from the sun by the active polymer layer and transform it into electrical power. Organic solar cells are advantageous than inorganic ones because of being low-cost, easy-to-use and proper for large scale applications.

In this project, it is aimed to produce organic solar cells by using specific amounts of carbon nanotube (CNT) doping.

According to this aim, it is detected by using the fluorescence spectroscopy that CNTs can be used in organic solar cells. Later, the homogenous distribution of doping SWCNT into donor material was displayed by AFM, and correct proportion of SWCNTs are chosen by those images. In order to increase the efficiency of organic solar cell SWCNT doped P3HT was used as donor molecule. The acceptor molecule was PCBM in here. Surface characterization of prepared samples was made by Atomic Force Microscope (AFM), while electrical characterization of them is done with airless environment cabin (glove-box) system in nitrogen environment.

As a result, devices prepared with addition of cyclohexanone in P3HT: SWCNT%:PCBM new load paths to carbon nanotubes were provided, as a result of the measurements short circuit current obtained was raised from the reference to 53%. The best yields were found as 2.24% in 0.2% SWCNT doped devices. This result shows efficiency is healed according to the reference rate as 64%.

In this study, certain amounts of carbon nanotube doped organic solar cells were produced, which are highly efficient rather than traditional organic solar cells and low cost, easy-to-produce rather than inorganic solar cells, by using environmentally friendly materials.

Key Words: Solar Power, Organic Solar Cell, Carbon Nanotube Dope, AFM

1. PURPOSE

Organic solar cell absorbs the light coming from the sun into the active polymer layer and transforms it directly into the electrical power. Organic solar cells are advantageous than inorganic ones because of being low-cost, easy-to-use and proper for large scale applications. In the project, it is aimed to produce certain amounts of carbon nanotube doped organic solar cells, which are highly efficient rather than traditional organic solar cells and low-cost, easy to produce rather than inorganic ones.

For this reason, in the study single walled carbon nanotube (SWCNT) doped P3HT were used as a donor molecule to increase the efficiency of organic solar cell. Furthermore, PCBM was the acceptor molecule. Surface characterization of prepared samples was made by Atomic Force Microscope (AFM), while electrical characterization of them is done with airless environment cabin (glove-box) system in nitrogen environment. In this study;

- Usage availability of carbon nanotubes (CNT) in organic solar cells determination with the help of Fluorescence Spectroscopy,
- Homogenous distribution determination of doped SWCNTs into the donor material by using AFM,
- Defining the correct proportion of SWCNT by AFM,
- Increasing the efficiency by doping SWCNT in organic solar cells was aimed.

2. INTRODUCTION

The increasing environmental pollution due to exhaustion of fossil fuel resources has led to an increase in the search of economically convenient, clean and renewable alternative energy source. Solar power is not only one of the unlimited energy source, but also has the potential that can provide the required energy that the world needs and prevents the energy crises.

Solar cells or photovoltaic (PV) cells transform the light they take from the sun into electrical power. Like each plant transforms the light they take from the Sun into chemical energy, “Organic cell” idea is inspired by the leaves.

When the first Si based p-n junction solar cells were produced in 1954, it proved low-cost and highly efficient solar cells can be made. First highly efficient GaAs based cells were produced by Zhores Alferov’s team, in 1970. 10% efficient $\text{Cu}_2\text{S}/\text{CdS}$ thin film solar cells were started to use in Delaware University, 1991. By GaInP/GaAs cells 30% efficiency was reached as a first time in 1994 and 40% efficiency barrier was achieved to exceed in 2006. While these developments in inorganic solar cells are reached, organic polymers attract the attention of scientists although they are low efficient. (Hoppe, 2004) Besides the inorganic solar cells, organic ones are the ones that researchers focus on because of the transparency, weight, flexibility and low-cost materials (Ergün, 2010).

Organic solar cells are environmentally friendly and have economical technology because of its simple production process and requiring less material to produce. Nevertheless, researches and innovations to be introduced in the technology are important in organic solar cell technology’s development (Liao, K.s, 2010).

Exciton’s (electron-hole pair) diffusion distance causes a huge problem since the organic solar cells were invented. As an example, exciton diffusion distance of poly (p-phenylene vinylene) polymer is determined shorter than 10 nm. When tiny amounts of SWCNTs are doped into donor material, it is seen that new leakage channels are formed. Thus, it not only increases the charge carrier’s mobility, but also provides the transfer of charge carriers (Biercuk, 2002).

2.1. ORGANIC SOLAR CELLS

Solar cells (OPV) are the devices that are basically transforming the light power into electrical energy in two steps. Firstly, semiconductor materials in the structure creates positive charged hole or negative charged electron pair (p-type and n-type) because of the absorption of light. Then, structure of the device is forced the electrons and holes to move to the terminals (electrons to negative pole, holes to positive pole), as a result it creates electrical power.

Recently, different materials usage in researches of solar cells is showing a rapid increase than the mostly used traditional inorganic semiconductors (Si, Ge, GaAs, etc). Organic solar cell is one of them.

Organic materials can be rendered easily at low temperatures in a cheap, easy, convenient and flexible structure to make a very thin film that stands out about these features. However, generally organic materials are insulators. This problem is solved with the usage of conjugated materials (polymers) in solar cell production, and it is possible with the pi orbitals of the optical absorption and charge carrier structures and it provides required properties that are significant in electrical power production of solar cells. (www.wikipedia.org, Organic Solar Cells)

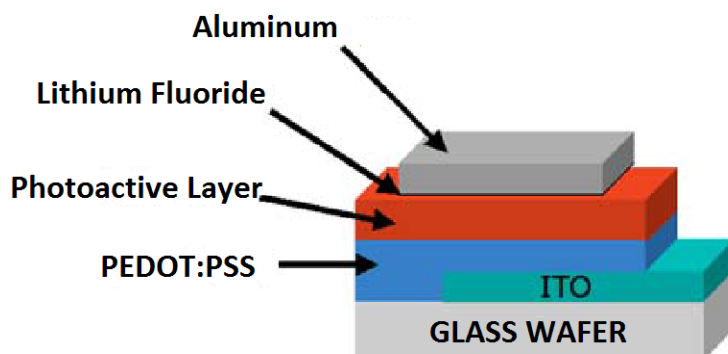


Figure 2.1. Organic solar cell structure (Hoppe, 2004)

2.1.1.OPV CELLS BASIC WORKING PRINCIPLES

Primer photons coming from the organic layer are absorbed by the p-type molecules which behave like a semiconductor, and it becomes a conductor with the excitation of moving charge carriers.

Semiconductor behavior of these molecules is caused from the structure of them. Each polymer and tiny molecule which is used in photovoltaic has a huge coupled system. In semiconductors, carbon atoms have single or double bonds.

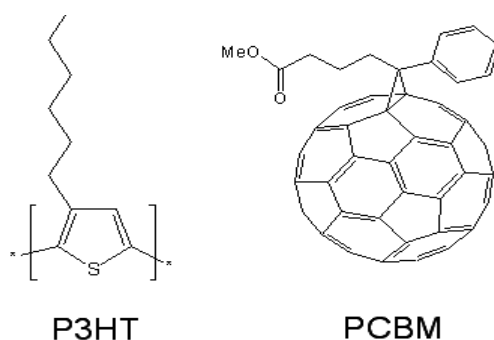


Figure 2.2. Structure of P3HT and PCBM (Tajima, 2008)

Those Hydrocarbon ones are placed into π orbits by P_z orbitals and do the electron exchange with the bond across it. This exchange is from HOMO (Highest Occupied Molecular Orbital) to LUMO

(Lowest Unoccupied Molecular Orbital). This empty region among these two energy orbitals is called the band gap. This band gap is about $\sim 1-4\text{eV}$.

In organic solar cells, photon absorption is not creating the free charge carriers by the free motion of electron and holes in related electrodes. In electron-hole pairs, electrons are attracted by the holes with the Coulomb force and create the excitons. For this reason, the bond between electron and hole is crashed by exciton dissolve. Excitons binding energy is not higher than the thermal energy in room temperature; this situation annihilates the probability of thermal breakdown.

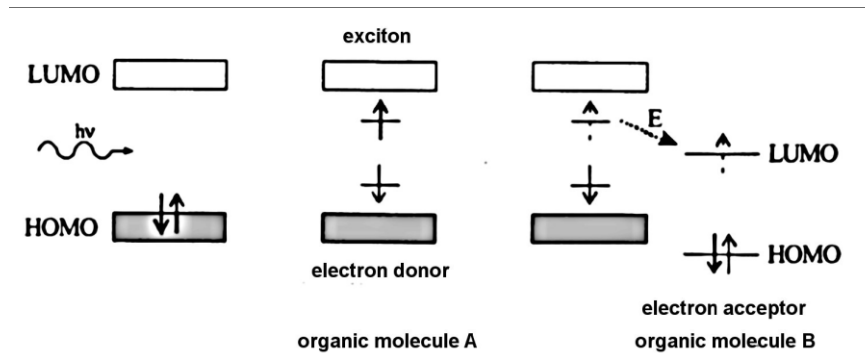


Figure 2.3.Charge carriage in organic solar cell

After the exciton separation, free charge carriers move to the related electrode, however this motion is slower than the inorganic semiconductors and related to the organic molecule structure.

About this application, organic solar cells are more advantageous than inorganic ones. Being low-cost and easy-to-produce is giving them an important role. Being transparent, flexible, thin and to adjust the band gap by the absorption of light are the significant properties of organic solar cells (Ergün, 2010)

By the absorption of excited exciton pair, a photovoltaic study begins. This charge creation doesn't take too much time as others. If the gap where the transition occurs is enough, there exists an electric field and it scatters electrons and holes into the related electrodes.

A small amount of energy which is needed to control the separated excitons in metal-semiconductor-metal structure is created with the impact of light energy. The factor that excites the system is ΔW ($W_{\text{anode}} - W_{\text{cathode}}$) here. Therefore, heterojunctions that has a difference among them is proper as donor and acceptor creation.

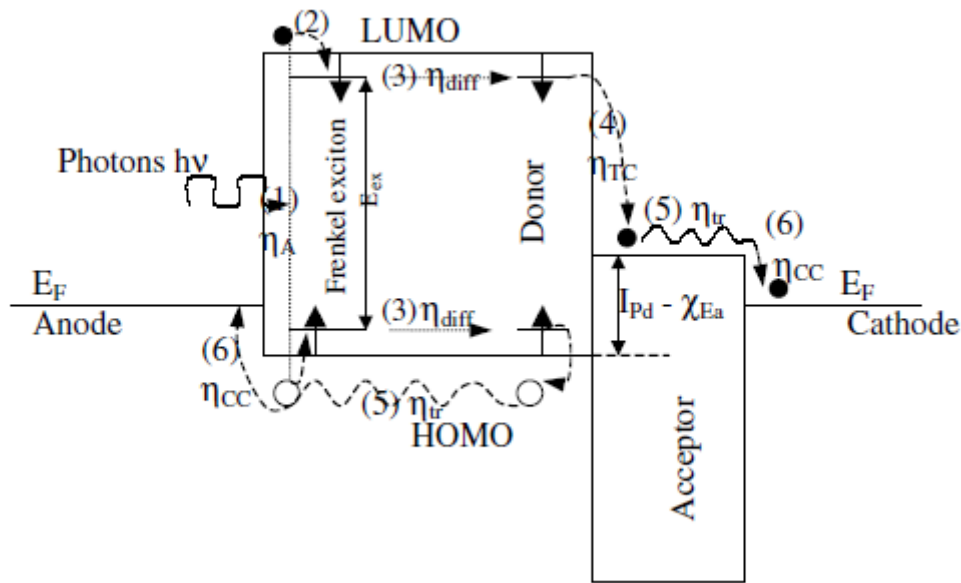


Figure 2.4. Charge creation and storage steps of an organic photovoltaic cell (Moliton, 2006)

It is summarized below the steps of the creation of charge carriers and its storage of an organic photovoltaic cell by the effect of light.

1. Photon absorption:

In p-type organic solar cells, light creates the electron-hole pairs to provide the electron transfer of the donor material from HOMO to LUMO. η_A depends on the optical absorption coefficient and the thickness of donor material.

2. Exciton Production:

Electron-hole production is caused from photo excitation. As a result, it is excited but neutral and short lasted. These are defined as excitons and there occurs a resulting energy. This energy is smaller than two bands. If we define the band gap as E_G , excitons binding energy is $E_G - E_{ex}$ (in organics it is around 0,1- 0,2 eV). These excited situations (LUMO by electron and HOMO by hole) are defined as the non-coupled excitons.

3. Exciton Diffusion (η_{diff}):

Förster (long range) or Dexter (among neighbor molecules) transfers can be between donor and acceptor molecules. $\eta_{diff} < 1$. Because, various recombination processes can produce thicker donor molecules.

4. Exciton Separation (η_{TC}):

If the diffusion length is enough, exciton is faced to an internal field, electron and holes are separated. Internal field produces donor-acceptor interfaces. When the LUMO level of acceptor is shorter than the excitonic situation that exists at the bottom of conduction band of a donor, it might create internal field at the donor-acceptor interface.

5. Charge Carriers Motion to Electrodes (η_{Tr})

This motion has the classical mechanism of organic materials. Mobility can be reduced because of the traps inside the material. Unless the charge carriers infinitely trapped (lattice degeneration), we can think $\eta_{Tr}=1$.

6. Charge Storage in Electrodes (η_{cc})

This situation occurs effectively when the conditions below are provided. $(E_F)_{cathode} < (E_{LUMO})_{acceptor}$ and $(E_F)_{anode} > (E_{HOMO})_{donor}$. When the conditions are whole fulfilled $\eta_{cc} \sim 1$. (Moliton, 2006).

2.1.2. OPV Cell Types

2.1.2.1. Single Layered OPV Cells

First OPV cells are produced by thermally evaporated organic molecular layer which is placed among two electrodes. These cells are generally known as sandwich and caused from the difference of carrier motions among anode and cathode. Single layered ones have the structure of metal-semiconductor-metal.

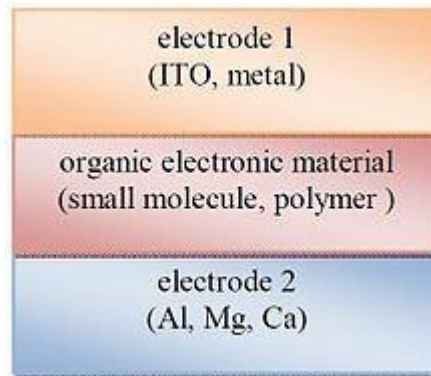


Figure 2.5. Single layered OPV cell (www.wikipedia.org, Organic Solar Cells)

Difference between two conductors creates an electric field in the organic layer. Because the organic layer absorbs the light, electrons move to LUMO and they leave holes in HOMO and create excitons. The tension caused from that difference helps the exciton pairs to separate. It repels electrons to positive and holes to negative pole. The current and tension produced in that process is effective in heterojunction based solar cells.

This kind of single layered OPV cells are not working properly. They have low quantum efficiency (<1%) and low energy transformation efficiency (<0,1%). The biggest problem is the electric field produced from the difference of two conducting electrodes is not enough to dissolve excitons. In order to deal with this problem, poly layered photovoltaic cells are developed.

2.1.2.2. Double Layered OPV Cells

This kind of OPV cells are produced from two different layers among two conducting layers. Two layers' electron affinities and ionization energies are different. Therefore, there exist electrostatic forces among two layers. This idea is an important step for OPV cells. They occur by the combination of electron donor (D) and electron acceptor (A) material layers. These two layers are covered by two electrodes like a sandwich. While the electrons are chosen, it is important to be proper to HOMO in donors and proper to LUMO in acceptors (Liao, K.S, 2010).

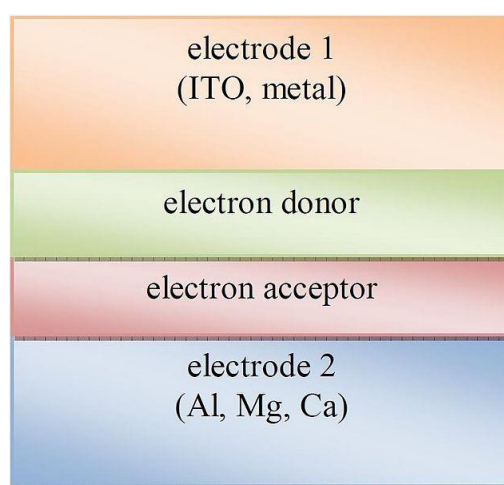


Figure 2.6. Structure of a double layered organic solar cell (www.wikipedia.org, Organic Solar Cells)

The biggest advantage of this system is the electron and hole easy motion into the suitable polymer material and to reduce charge pairs. Thus, charge carriers move to the donor and acceptor effectively by separating. 1% efficiency was reached by the first production from Tang, in 1986 (Liao, K.S, 2010). Exciton diffusion length is around 10 nm in organic electronic materials. To separate the charge carriers in most excitons, the diffusion lengths of layers and diffusion thicknesses should be the same. However, polymer layers should have the thickness around 100 nm to absorb enough amount of light. Only some amount of excitons can be dissolved with that thickness. In order to deal with this problem, a new heterojunction photovoltaic cell is designed.

2.1.2.3. Volumetric Heterojunction Solar Cells

It is the system where OPV active layer works properly. In this kind of photovoltaic cells, electron donor and electron acceptor is mixed and prepared a new polymer. The highest efficiency in OPV cells is caught with the help of that active layer. In that composite structure, donor (hole motion) and acceptor (electron motion) materials are not in the superficial structure. While the electrons move to the acceptors and caught by the electrode, holes move the opposite direction and caught by the other electrode (Liao, K.S, 2010).

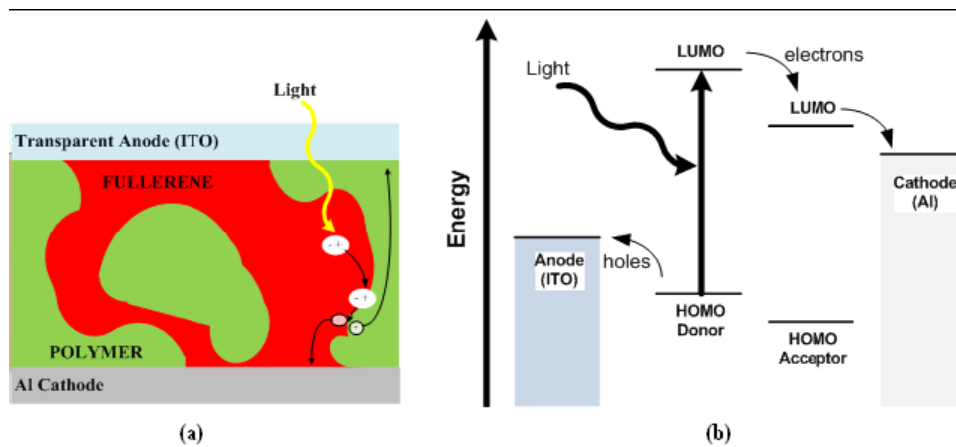


Figure 2.7. a. BHI cell structure scheme

b.BHI OPV cells band gap diagram (Liao, K.S, 2010)

OPV cells collect small amounts of excitons which donors and acceptors create. Composition of donor and acceptor based volumetric heterojunction solar cells are advantageous because of having a large contact area of donors and acceptors.

2.2. CARBON NANOTUBES (CNT)

Nanotubes have the properties that most different materials show by themselves. It is expected to find new nanotube application fields like quantum wires, diode and transistors, soon. They show many more physical and mechanical properties. As an example, nanotubes are very durable, highly flexible, and plastic can become a conductor by doping it with nanotubes (Koç, 2003).

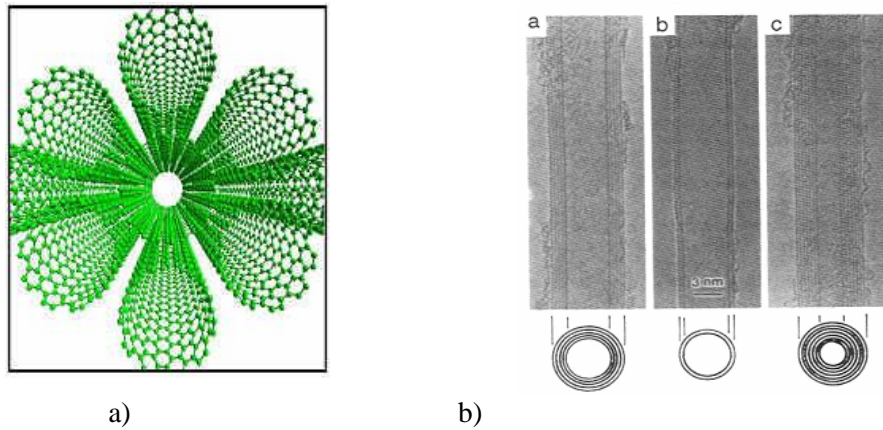


Figure 2.8. a) Single walled CNT b) Poly walled CNT (Koç, 2003)

2.2.1. Carbon Nanotubes Structural Properties

By high resolution microscopy techniques, the structure of carbon nanotubes is being investigated. As a result of these experiments, it is understood that carbon nanotubes are having cylindrical structure with crystal graphite in hexagonal lattice. There can be 3 kinds of nanotubes: “armchair”, “zigzag”, and two dimensional graphite slabs depending on how you roll “chiral”.

2.2.2. Carbon Nanotubes Electrical Properties

One carbon sheet is a semi-metal. This means that it has some properties like a semiconductor and a metal. When a graphite sheet is rolled a formed a nanotube, around the circle there is not only carbon atoms in order but also electrons quantum mechanical wave functions are adjusted properly. In radial directions, electrons are limited by the single layered graphite sheet and they are made thinner. Periodic boundary conditions around the circle of nanotube are revealing. For example, if a nanotube has 10 hexagons around a circle, 11th hexagon is overlapped with the 1st one. There is a 2π phase difference around the cylinder (Koç, 2003).

If two nanotubes which are non-identical because of small differences are added end to end, addition point is behaved like an electrical circuit named diode. Diodes are generally used in transforming the alternative current to direct current and be the fundamental of rectifiers (Zettle, 2008).

Another exciting research is about the transistors which are the fundamental structures of integrated circuits. In the future with the usage of nanotubes in circuits, it will be inevitable to produce transistors. Independent poly layered nanotubes and mono layered nanotubes based transistors are like “Field Effect Transistors (FET)”. When we cool down a FET from a room temperature to 4 °K, behavior of

the circuit is changed. This circuit behaves like a FET at room temperature, whereas it behaves like a “Single Electron Transistor (SET)” at 4°K. (Koç, 2003).

2.2.3. Carbon Nanotubes Mechanical Properties

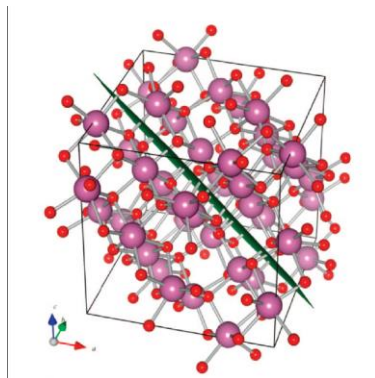
Another research area is the mechanical properties of carbon nanotubes. It is expected that nanotubes should be very durable and highly flexible because of consuming graphite and carbon fibers. Also, mono layered carbon nanotubes are expected to be quite durable and it shouldn't break under a stretch like the carbon fiber in space technology applications. A nanotube can be highly extended without a cleavage. In contrast to the carbon fibers, mono layered carbon nanotubes are quite flexible. They can be twisted, straightened, rolled as small circles or as a result of other various stretches it can remain durable. Furthermore Bernholc et al. observed that when the stress on nanotube is vanished it takes its previous original shape. In contrast to the easily breaking carbon fibers under stress, carbon nanotubes provide the only flexible structure (Bernholc et al., 1997).

2.3. OPV Cell Materials; Electrodes and Organic Molecules

2.3.1. Indium Tin Oxide (ITO)

Indium Tin Oxide is a transparent conductor. It is produced by covering the Tin by Indium oxide. Tin covered indium oxide is generally used as electrode in organic cells. It is preferred because of being highly conductive, having permeability to visible light, having a large band gap, and having large scale applications (Ergün , 2010). ITO is an n-type material. It has metal features because of having charge carrier density of 10^{21}cm^{-3} . When the doping is increased, its conductivity increases as $10^{-4}\Omega^{-1}/\text{cm}$, however it loses the transparency. Resistivity of ITO is around $10^{-4}\Omega/\text{square}$.

a)



b)

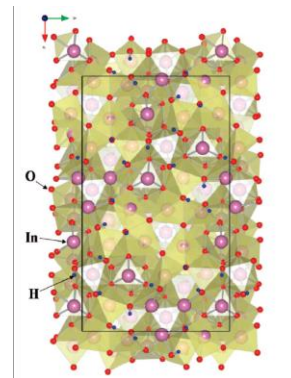


Figure 2.9. (a) In_2O_3 crystal structure (b) ITO atomic structure (Ergün D., 2010)

Having a good transparency in visible region of ITO, high electrical conductivity, tight substrates binding are the needed properties of OLEDs (organic light emitting diodes) and OPV cells. (Ergün D., 2010).

2.3.2. PEDOT: PSS

Poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT: PSS), is prepared by mixing two isomers into a conducting polymer (Figure 2.10.). PEDOT is polymer based polythiophene. Whereas PEDOT is not a conductor, by doping the polythiophene part of it properly it became a good conductor. PEDOT is an insoluble material in itself. However, when it is synthesized with PSS, you can get a juicy distribution. Polycationic PEDOT chains are solved into polycationic PSS chains and hold the charges by them.

In OLED and OPV cells, PEDOT: PSS is generally used as buffer layer among organic material and ITO in anode, because of high conductivity and transparency in visible region. PEDOT chains are imaged as short rods. It is guessed as in most semiconductors, PEDOT: PSS increases compliance of HOMO and decreases working function of anode (Ergün D., 2010).

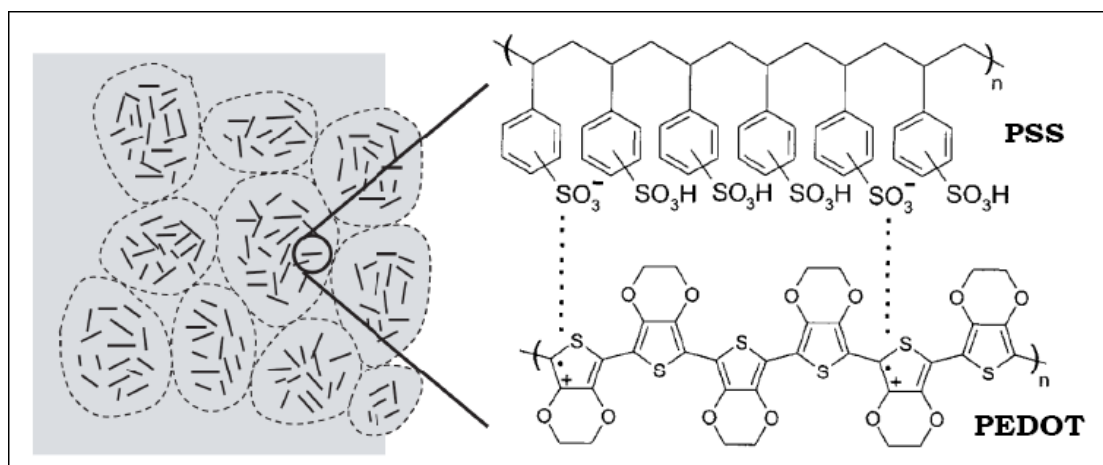


Figure 2.10. Left: PEDOT: PSS particles seen from the top. PEDOT chains are like short rods, they are covered by thin PSS surface. Right: Chemical form of surface (Ergün D., 2010)

PEDOT:PSS resistivity is about ≈ 45 k Ω /square. Moreover, PEDOT: PSS reduces short cuts by the softening effect of surface roughness of ITO (Ergün D., 2010).

2.3.3. Poly(3-hexylthiophene 2,5 diyl (P3HT)

P3HT is a mixture of polythiophene based. Electron behaves as donor light absorber in solar cells. Its HOMO level is -5.2 eV which is closed to PEDOT: PSS and ITO. LUMO level is -3,5 eV.

2.3.4. [6,6]-phenyl-C61 butyric acid methyl ester (PCBM)

PCBM is a derivation of fullerene, and it can be acceptable till 6 electrons. Fullerene types provide maximum 6 electron motions, at which organic thin films has $0,5 \text{ cm}^2/\text{Vs}$ value. In pure PCBM film, electron mobility is measured as $10\text{-}3 \text{ cm}^2/\text{Vs}$. PCBM's HOMO is $-5,9 \text{ eV}$, while LUMO is -3.73 eV .

2.3.5. P3HT:PCBM Mixture

P3HT:PCBM, is generally used for producing volumetric heterojunction OPV cells, and it is mixed for creating donor-acceptor pairs. In OPV cells, while P3HT is the electron giving part, the electron acceptor part is PCBM. In mixture of P3HT:PCBM, electrons mobility is $7.7 \times 10^{-5} \text{ cm}^2/\text{Vs}$, hole mobility is $5.1 \times 10^{-5} \text{ cm}^2/\text{Vs}$.

P3HT:PCBM results are not faced in organic cell materials which is 5%. PCBM is a kind of fullerene and in most organic cells it is electron acceptor. P3HT come the family of Polythiophene, which is kind of a polymer and gives the mixture a photovoltaic effect (Ergün D., 2010).

2.3.6. Single Walled Carbon Nanotubes (SWCNT)

The SWCNTs we used are provided from Cheap Tubes firm. The table below it is showing the SWCNT properties.

Table 2.1 CNT properties that are used for doping

SWNT outer diameter	1-2 nm
SWNT inner diameter	0.8-1.6 nm
SWNT purity	>90 wt%
Addition MWNT content	>5wt%
Amorphous carbon content	<3wt%
SWNT length	0,5-2,0 μm
SWNT specific surface area	407 m^2/g
SWNT electrical conductivity	>100 S/cm
Bulk intensity	0,14 g/cm^3

2.4. TOOLS USED

2.4.1. Atomic Force Microscope (AFM) (Ambios Technology, Q-Scope Series)

Binnig, Quate and Gerber invented it in 1986. It is named as microscope but not like the ordinary microscopes we know. Ordinary ones show the image of an object in its real sizes. However, atomic force microscope gives the image of understanding how the surface of an object. It means, you can't see really the molecule, but only understand the sizes or arrangement of a molecule.

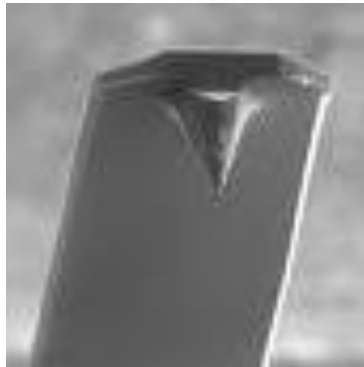


Figure 2.11. AFM tip (www.wikipedia.org, Atomic Force Microscope)

Atomic force microscope is a system which you can examine the force interactions of a nano sized needle like probe with the interaction of any surface. Generally it has two types, which are “contact” and “noncontact” modes. General aim of usage is getting 3 dimensional images of surface, nanolithography, surface roughness determination, morphology analysis in nanometric sizes.

Contact Mode: This is the first mode of atomic force microscope. Tip works like a gramophone needle; while the tip is scanning the surface to be examined, it shows a tiny force (in nanonewton scale). The force wants to be balanced during the scanning, so the surface image is got. The sensitivity of this mode is around some nanometers.

The most important thing here is the tip material, it is required to be so thin. In reality, tip doesn't consist of a single atom; it is quite hard to take an image of a single atom with this method since many atoms are interacting with each other in some defined curvature.

Despite all these, the biggest advantage of that method is it doesn't require any special environment. Surface image can be taken by that device even inside a liquid or outdoors.

Noncontact Mode: This is a renewable model of a contact mode, and it depends on the principle that having a resonance by the vibration of arm's natural vibration frequency. Arm and the tip attached to it is closed to the surface without touching and started to scan, by doing this the force on the tip wants to be stabilized and so that surface image is taken. Sensitivity of that mode is like the contact mode. In some cases (like a more sensible tip, well-adjusted electronical or mechanical system), it even becomes better.

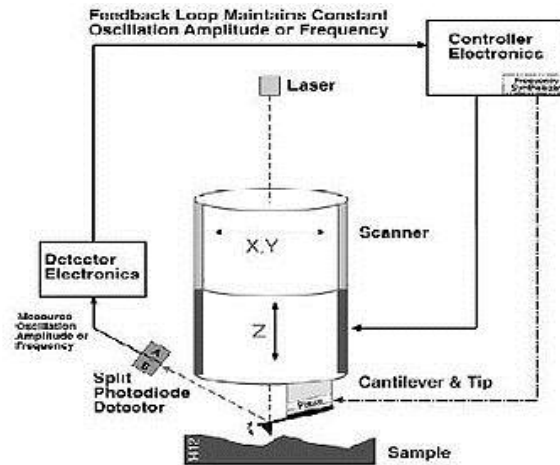


Figure 2.12. AFM working principles (www.wikipedia.org, Atomic Force Microscope)

AFM noncontact mode

Application Fields

- Creates topographic images of surfaces.
- Helps to understand some materials are in the environment or not.
- Atoms location on the surface can be changed.
- Understanding the characteristics of a material.

(www.nanoturkiye.net)

2.4.2. Spin Coater (Laurell, Ws-400b-6npp-lite)

Spin coating is used for applying thin films on flat surfaces. It placed on the base which is rotated with a high speed, and liquid is spread around it with the high centrifugal force. The machine provides a spin coating is called spinner.

Spinned film is rotated till the desired thickness is provided at the edges of a liquid surface. Applied solvent is generally volatile, so it evaporates at the same time. So, it becomes a thin film by doing a high speed centrifuge thickness of the film also depends on the concentration of solvent.

Common micro production of spin coating is used for preparing thin films thinner than 10 nm. Deposit layers about 1 micrometer thick is used as photolithographic concentration. Resists generally have curvatures at 20-80 rotational speed in 30 to 60 seconds. This method is used often because of obtained thickness of spin coating. The coatings can show the properties like self-cleaning on those thin films. Transparent Titanium dioxide shows its properties in the production of thin films on the quartz wafers.



Figure 2.13. Spin Coater

2.4.3. Fluorescence (Edinburgh Instruments, Epled 360)

Radiation from a continuous or discrete light source is absorbed and disturbed atoms change their energy levels from excited to fundamental level and creates radiation. Measuring this is the principle of fluorescence spectroscopy.

From 1960s, it had been working on analytical methods which are related to atomic fluorescence. It had been seen that, atomic fluorescence technique is suitable for defining elements quantitatively. However, it isn't common as atomic absorption or atomic emission techniques. The reason of that is they became famous before the atomic fluorescence technique and the devices of them are expensive and hard to understand the usage.

Fluorescence Types:

There are 5 important types of atomic fluorescence which are:

- 1) Resonance fluorescence
- 2) Directloop fluorescence
- 3) Graded fluorescence
- 4) Thermal mounted fluorescence
- 5) Multiphoton fluorescence (Anadolu Üniversitesi Yayınları, 2010).

3. MATERIAL AND METHOD

Our studies were performed in Ege University Solar Power Institute laboratories.

3.1. Preparation of Film/Solvent for AFM Surface Analysis

Having the maximum efficiency of the new organic solar cell is related to have the most proper morphological structure in atomic level. AFM results were got by noncontact mode of AFM, by scanning 8 μm x 8 μm area at 1024 resolution. The most proper solution for organic solar cells was chosen with the help of images got. In the first trials, glass is used as a substrate.

3.1.1. Wafer Cleaning

In the beginning of our project, glasses were cut in sizes of 25mm x 25 mm. Wafers were vibrated in ultrasonic cleaner for 15 min as an order of acetone, isopropanol, distilled water, and then dried with azot gas. Finally, glasses were cleaned in oxygen plasma under 200W for 2 min.

3.1.2. Preparing Solutions

Solutions prepared for our trials are shown below in the table. According to the literatures, pellets of SWCNTs are prevented by acetonitrile and cyclohexanone solutions.(Lu, 2012).

Table 3.1 Solvents prepared for AFM surface analysis

Soluble Molecule	Solvent	Concentration	Mixing Time
SWCNT on Mica	Dichlorobenzene	20 mg/mL	1 night
P3HT:CNT	Dichlorobenzene	20 mg/mL	1 night
P3HT:CNT	Dichlorobenzene: Acetonitrile (10:1)	20 mg/mL	1 night
P3HT:CNT	Dichlorobenzene: Cyclohexanone (10:1)	20 mg/mL	1 night

3.1.3. Spin Coating

Solutions are coated on glass surface for AFM analysis. This process occurred in two steps. In the first step, solutions are coated on glass for 1000 rpm. In the second step, coated solution dried at 1500 rpm for 30 seconds.

3.2. Device Preparation

3.2.1. ITO Layer Preparation (Delta Technologies, LTD)

ITO coated glasses cut in sizes of 25mm x 25 mm. Roughness of ITO surface is around 0,4-0,6 nm. ITO layer was etched from one side for 5 mm width, which was used as an electrode. For that etching process, diluted hydrochloric acid (HCl) and nitric acid (HNO₃) were used. ITO etching solution composition was HCl:HNO₃:H₂O (4,6:0,4:5).

ITO surfaces cleaned in ultrasonic bath for 15 minutes with an order of acetone, isopropanol, and distilled water, then dried with nitrogen gas. Finally, ITO surfaces cleaned in oxygen plasma for 2 minutes under 200 W.

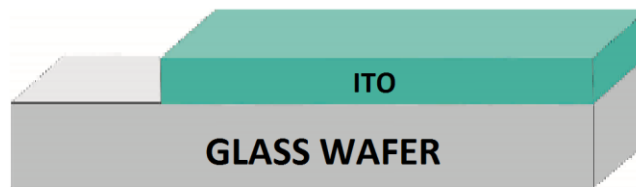


Figure 3.1 One side etched by acid ITO-glass layer

3.2.2. Spin Coating PEDOT:PSS (Heraeus-Clevius Metal and Technologies)

For making the device, PEDOT:PSS is coated with 4000 rpm Argon gas for 1 minute on ITO electrode. From the other side of PEDOT:PSS substrate, 5 mm width rectangular piece was removed. While PEDOT:PSS was etching, distilled water and cotton covered rod was used. Later, substrate was left in vacuum oven at 120°C, 30 minutes long for drying.

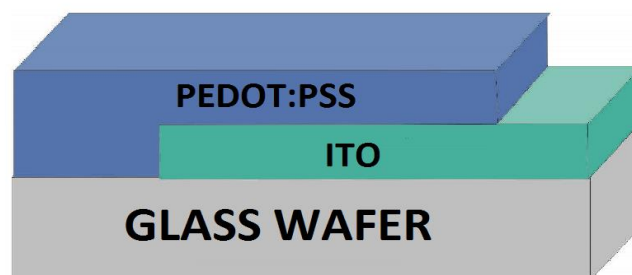


Figure 3.2. PEDOT:PSS coating

3.2.3. Photoactive Layer Preparation

Photoactive layer in organic solar cells is consisted of single or more layers, or from the mixture of photoactive organic molecules mixture. Organic molecules in that layer behave as donor or acceptor. The products got from those experiments are compared with each other and the most proper molecules or ratios are determined for the efficient photoactive layer.

The best results got with cyclohexanone in AFM, so we continued making devices with using 10% cyclohexanone. P3HT, PCBM and SWCNT are dissolved in 20 mg/ml dichlorobenzene. SWCNT doped in P3HT and added cyclohexanone in it. Later 1 night mixing, a reference solution without doping SWCNT and cyclohexanone mixture of P3HT:PCBM solution was prepared.

3.2.4. Spin Coating and Etching Process of Active Layer

The solutions prepared in previous steps are spin coated by 1000 rpm with Argon gas for 1 minute on ITO/PEDOT:PSS layer. ITO/ PEDOT: PSS/ P3HT: PCBM substrates same size, 5 mm width area is removed with the help of cotton rod and dichlorobenzene. The reason of that etching is to make a conductive surface for Al electrode which is evaporated on the surface in the later steps. Coated substrates were annealed at 120°C for 30 minutes and then were dried for 30 seconds at 1500 rpm.

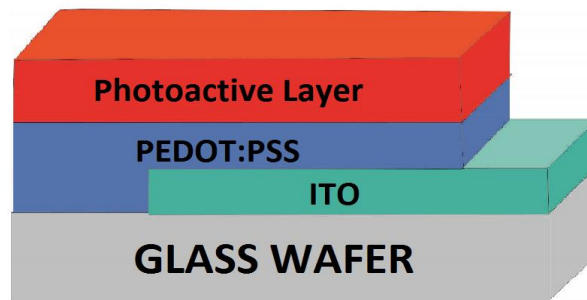


Figure 3.3 Photoactive layer coating

3.2.5. Lithium Fluoride and Aluminium Coating

After coating active layer on ITO/PEDOT:PSS surface, in order to complete the organic solar cell the LiF/Al was evaporated under vacuum as a cathode. LiF coating was 6\AA thick and at $0,1\text{ \AA/s}$ speed, whereas Al coating was 70 nm thick and at $1,2\text{ \AA/s}$ speed.

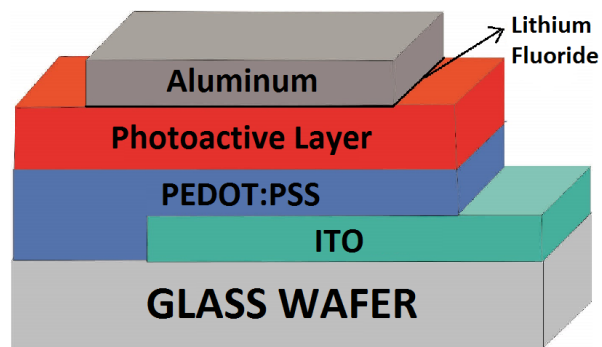
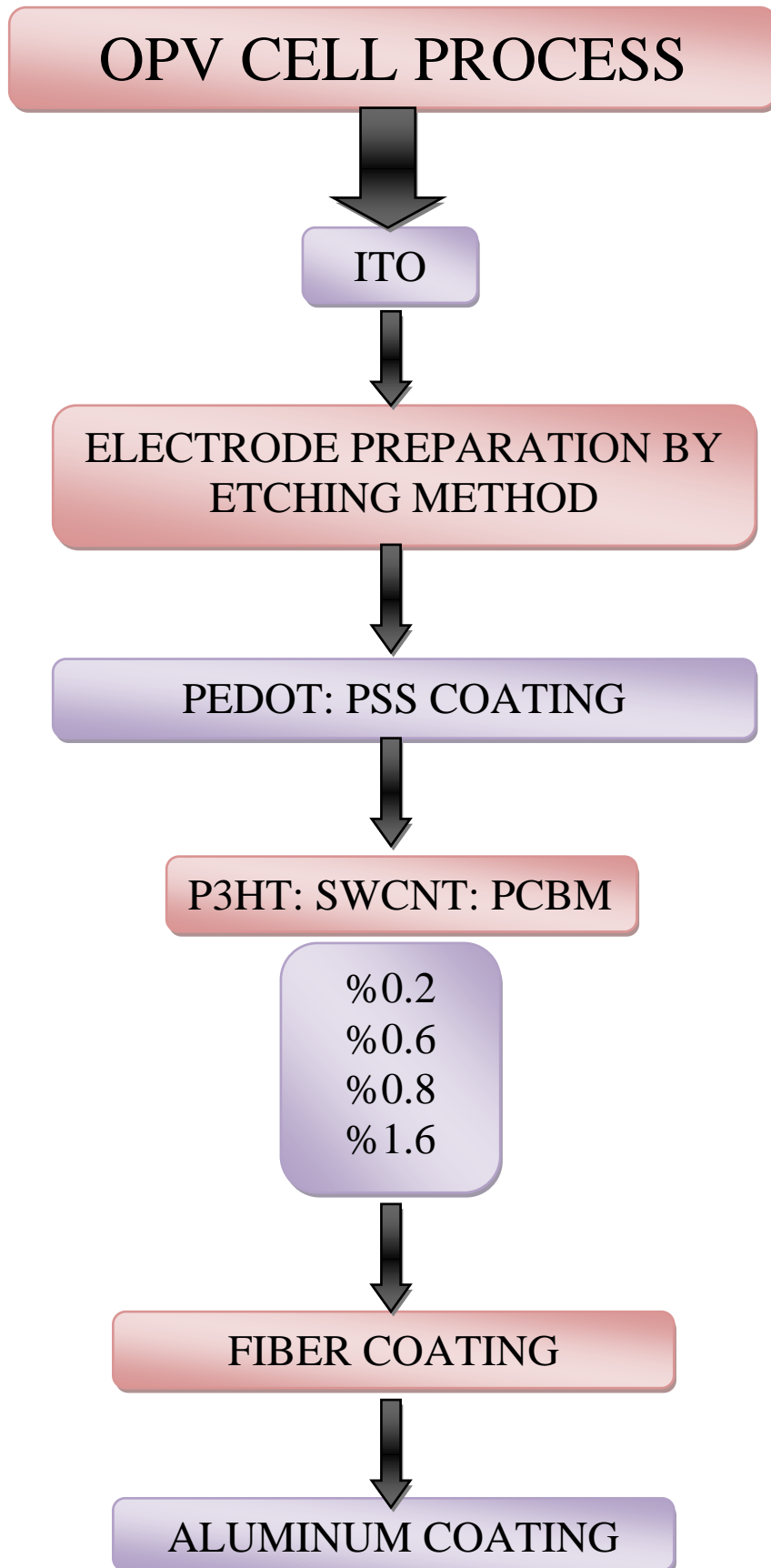


Figure 3.4 Lithium Fluoride and Aluminium coating

EXPERIMENT PROCESS SCHEME



4. RESULTS AND DISCUSSION

Fluorescence spectroscopy method results are in figure 4.1 graph. This measurement is repeated with 0.001 M P3HT which is doped with SWCNT at a similar concentration. As it can be seen from the graph, when the dope rate is increased the fluorescence effect is decreased, annihilated. The reason of that is because having an electron transfer from P3HT to SWCNTs. This result is a proof of SWCNT doped P3HT continues electrical transfer inside the device and you can use SWCNTs in photovoltaic cells. From the graph, maximum fluorescence effect is at 585 nm wavelength and there became a shoulder at 675 nm wavelength. SWCNTs interaction with P3HT is provided SWCNTs properties to be examined and gives availability to use them in device preparations.

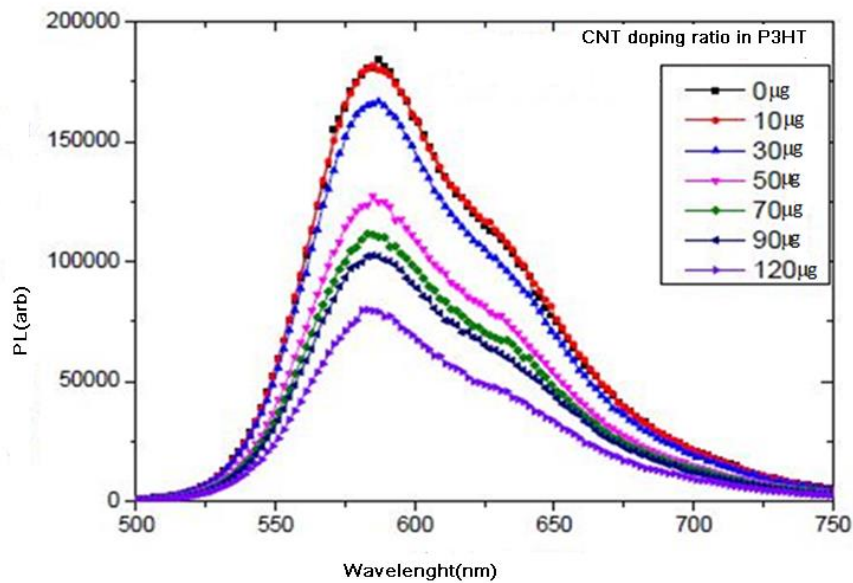


Figure 4.1 Fluorescence spectroscopy results

4.1. AFM Analysis

4.1.1. SWCNT and P3HT:CNT Comparison on Mica

2mg/ml concentration of dichlorobenzene solution is prepared for imaging carbon nanotubes. The biggest problem with the SWCNTs is they attract each other in seconds and create micron sized pellets. To prevent these pellets and image nanotubes properly, the solutions is vibrated in sonic vibrator for 5 minutes and without losing time it is spin coated on mica at 4000 rpm. At figure 4.2, thicknesses of SWCNTs vary from 30 nm to 400 nm; when we doped 10% volumetric rate of nanotubes in P3HT thickness changed from 300 nm to 400 nm. Also, pellets height reached to 353 nm. This shows P3HT coated SWCNT surface.

Surface structure has an important role in device performance. If the surface has high hills, charges tend to transfer from the tips of them and because of the overcharging regions where those hills are corrupted. Therefore, by doping SWCNT occurring pellets higher than 300 nm makes the efficiency of devices to be decreased and creates a broken morphology.

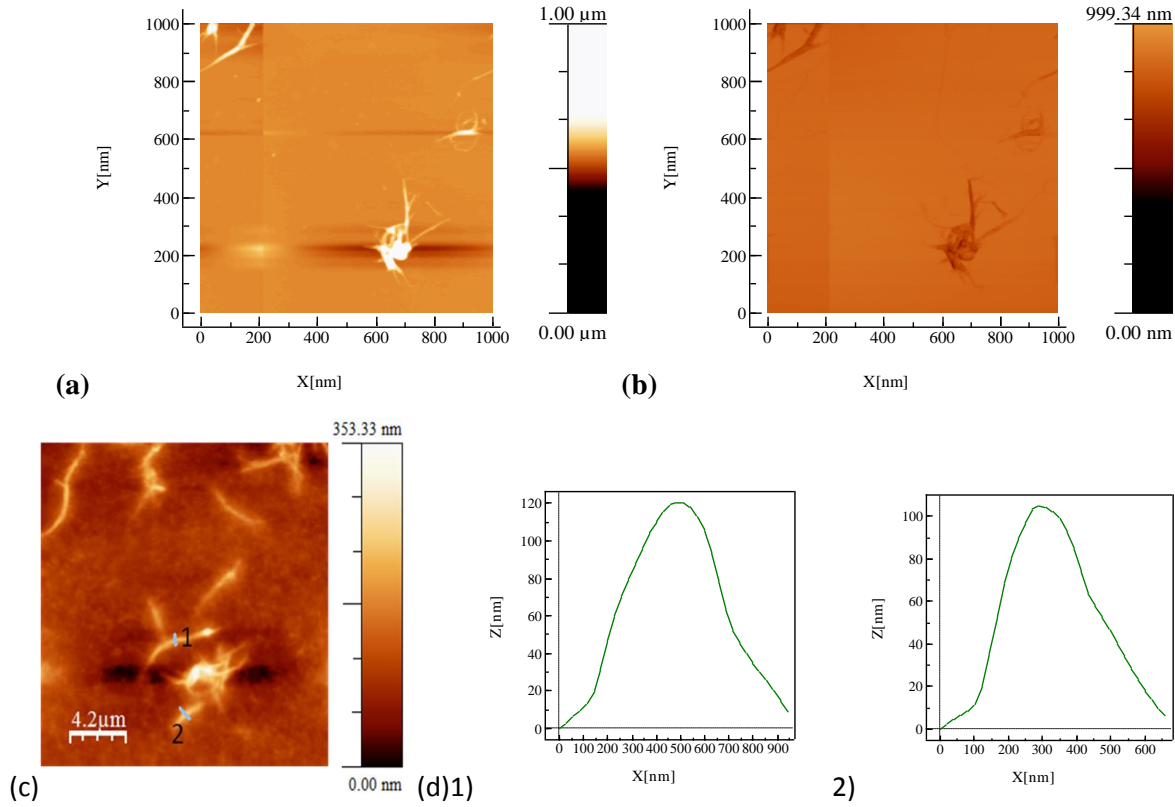


Figure 4.2 SWCNT and P3HT:SWCNT comparisons AFM analysis on mica

(a) SWCNT topography on mica (b)) SWCNT phase topography on mica

(c) P3HT:SWCNT topography (d) Sizes of pellets existed

Table 4.1 SWCNT and P3HT:SWCNT comparisons AFM roughness values on mica

Surface	RMS Roughness(μm)	Roughness Average (μm)	Average Height(μm)
SWCNT on mica	0.0228	0.0064	0.5612
P3HT:CNT	0.0402	0.0221	0.4739

4.1.2. Dichlorobenzene:Acetonitrile or Cyclohexanone (10:1) Solutions Effect on the Morphology on %3 SWCNT doped P3HT

Surface healing process is done before device preparation. Purpose here is to attract carbon nanotubes and to prevent pellets.

Way to do this is to defeat Van der Waals interactions among carbon nanotubes, and to create π - π pellet with P3HT of carbon nanotubes. Surface healing is examined with 3% doped P3HT with 10:1 added acetonitrile or cyclohexanone.

Figure 4.3.a shows acetonitrile, Figure 4.3.c shows cyclohexanone added surfaces topography. Dichlorobenzene: Acetonitrile (10:1) ratio prepared films surfaces has 300 nm height and more than 4 microns tall SWCNT pellets are imaged. Diameters of those pellets can be change to 1 micrometer. This shows us around 500 carbon nanotubes makes groups. The high roughness of 17.68 nm which SWCNT pellets make shows us acetonitrile is not proper for that process.

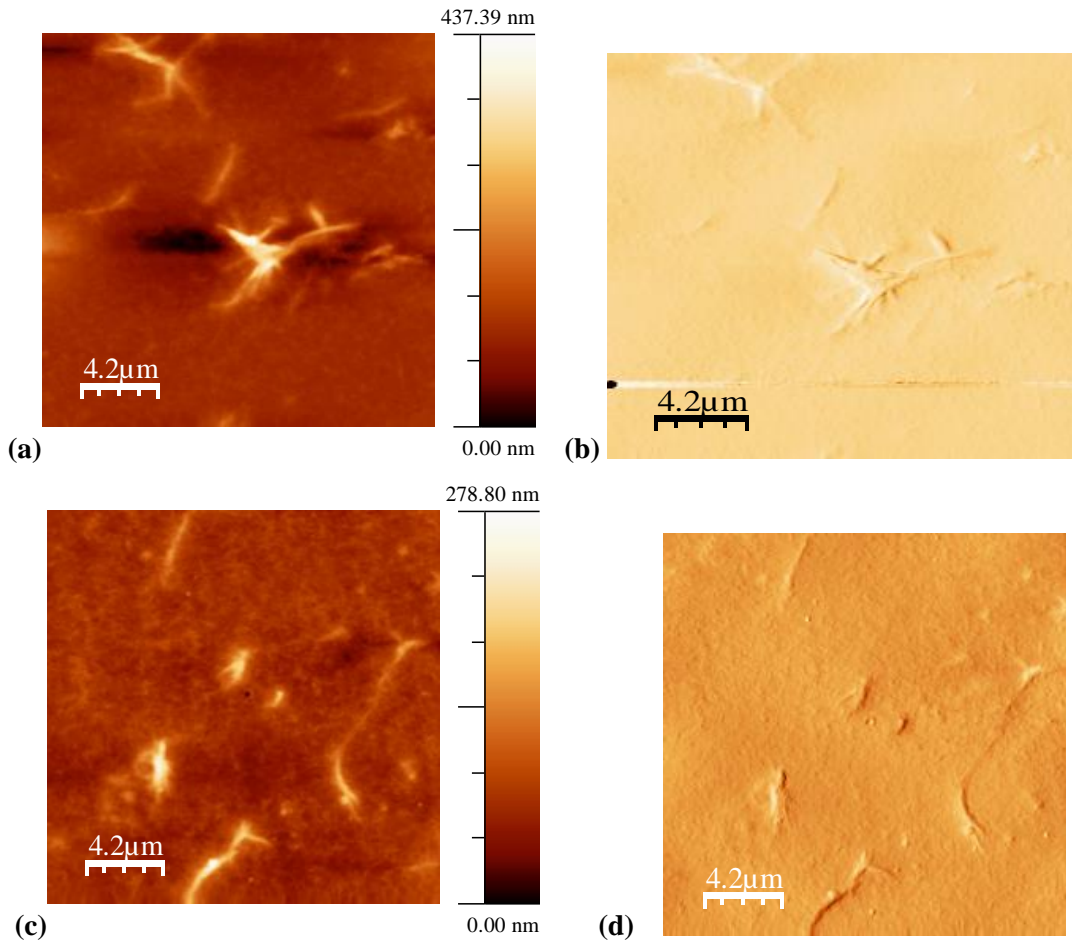


Figure 4.3 Dichlorobenzene: Acetonitrile or Cyclohexanone (10:1) solvents AFM results
(a) Dichlorobenzene: P3HT: CNT topography in acetonitrile solvent (b) Dichlorobenzene: P3HT: CNT phase topography in Acetonitrile solvent (c) Dichlorobenzene: P3HT: CNT topography in cyclohexanone solvent (d) Dichlorobenzene: P3HT: CNT phase topography in cyclohexanone solvent

Table 4.2. Acetonitrile or cyclohexanone (10:1) solvents AFM roughness values

Surface	RMS Roughness (nm)	Roughness Average(nm)	Average Height(nm)
SWCNT inside Acetonitrile	32.7	17.68	109.65
SWCNT inside cyclohexanone	20.03	12.21	75.73

Compared to acetonitrile, cyclohexanone based films splitted carbon nanotubes much better. The maximum height is 170 nm, average height is 75.73 nm and average roughness is decreased to 12.21 nm. Solution became more concentric like a gel with the addition of cyclohexanone in P3HT. As a result, P3HT molecules prevents pellets by covering the SWCNTs and keeping them apart.

4.1.3. P3HT: PCBM :SWCNT

SWCNT doped Al/P3HT:SWCNT:PCBM(1:X%:1)/PEDOT:PSS/ITO X:0.2, 0.4, 0.8,1.6 and 2.4 devices' efficiencies are shown in Figure 4.5. P3HT:PCBM (1:1) devices' efficiency of 1.36% is used as a reference, while P3HT is volumetrically doped 0.2% ratio ones have an efficiency is raised to 64% and found 2.24%. Having a rise in efficiency by doping is caused from shortcut current is healed to 53%. Current density (J_{sc}) is 4.79 mA/cm² in a reference organic solar cell, whereas 0.2% doped carbon nanotubes system has 7.32 mA/cm². However, the doping rate raised, the efficiency decreased. Volumetrically 0.6% ratio doped one efficiency is 1.74%, while 0.8% ratio doped one efficiency is 1.70% and 1.6% doped one has 1.59% efficiency.

There isn't an important change in shortcut currents of doped devices, but open circuit voltages V_{oc} are decreased with the dope rates inversely. This decrease in V_{oc} is related to the change in morphology. AFM is used for morphology analysis of P3HT:SWCNT:PCBM devices. (look at figure 4.6) 0.2% doped devices surfaces are coated properly, but when the doping rate is increased rate of forming groups also increased. In order of 0.6%, 0.8%, and 1.6% doped SWCNTs maximum heights are 42 nm, 60 nm, and 73 nm. These pellets increased not only the surface roughness but also the average height. As a result of this, V_{oc} is decreased as the dope ratio is increased.

IPCE (Incident Photon to Charge Carrier Efficiency) device was used in determination of outer quantum efficiency. By sending photons with different wavelengths to 4 mm² area of cells' active layer, it is defined that how many charge carriers can this system produce. In the reference cell, there exists hills at 360 nm and 480 nm, and a shoulder at 600 nm. At these wavelengths, reference outer quantum efficiencies are in order of 24%, 28% and 10%, 0.2% doped SWCNT outer quantum

efficiencies are 28%, 41% and 18.7%. Having flat regions at 0.6% doped devices helped to have higher outer quantum efficiencies. However, in more higher doping rates it is decreased because of distributed morphological defects on the surface.

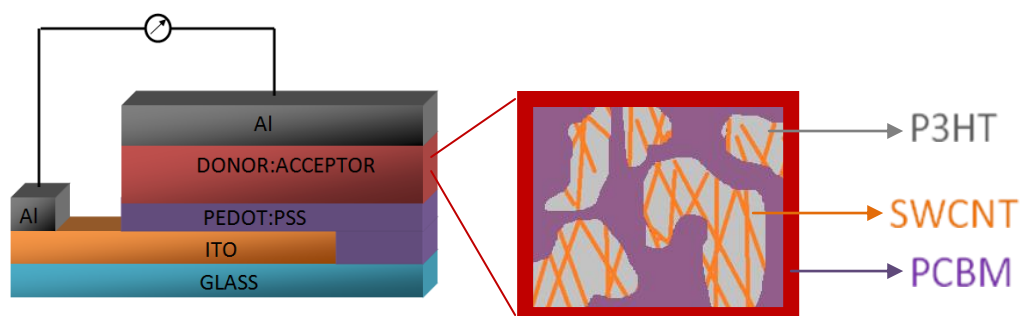
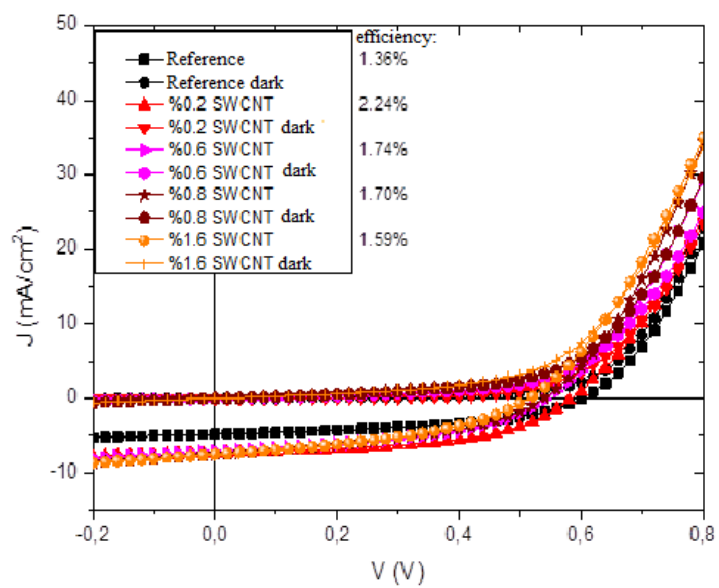
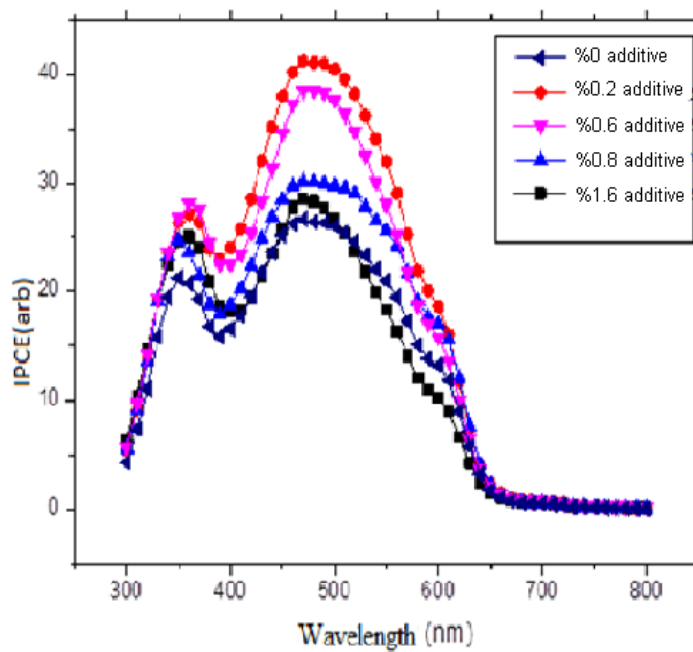


Figure 4.4 Schematizing donor and acceptor molecules



a)



b)

Figure 4.5 Doped devices a) current- voltage curve and b) IPCE analysis

Table 4.3 Efficiency values of produced CNT doped devices

Dope rate %	V _{oc} (mV)	J _{sc} (mA/cm ²)	FF	Efficiency %
0	600	4.79	0.47	1.36
0.2	580	7.32	0.52	2.24
0.6	540	7.14	0.45	1.74
0.8	540	7.49	0.41	1.70
1.6	520	7.49	0.41	1.59

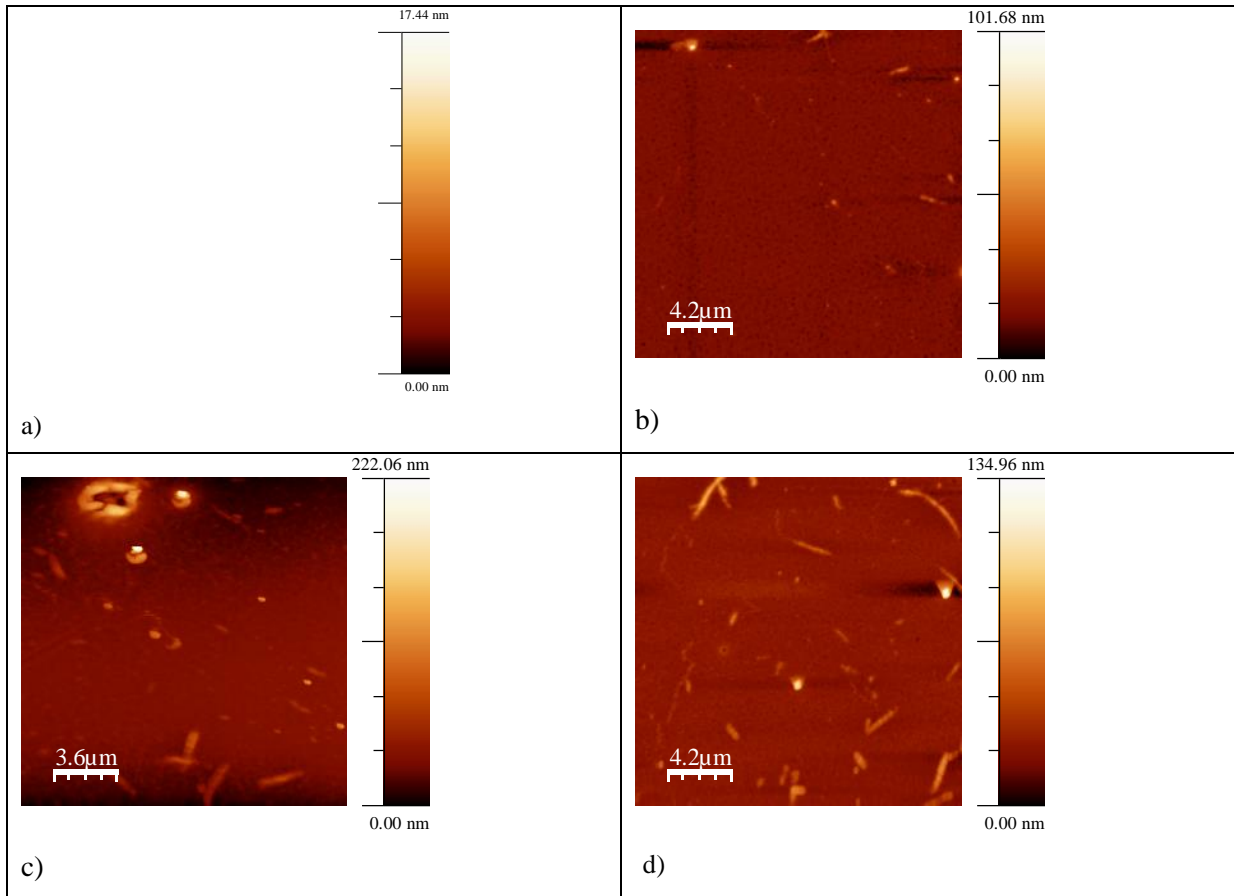


Figure 4.6 Different dope rates of Al/P3HT:SWCNT:PCBM (1:X%:1)/PEDOT:PSS/ITO devices AFM images
a)X:%0.2, b)X:%0.6, c)X:%0.8 and d)X=%1.2

Table 4.4 Different dope rates of Al/P3HT:SWCNT:PCBM (1:X%:1)/PEDOT:PSS/ITO devices AFM results roughness values

P3HT:SWCNT%:PCBM SWCNT doping rate	RMS Roughness (μm)	Average Roughness (μm)	Average Height (μm)
%0,2	0.98	0.72	3.82
%0,6	2.45	1.32	14.51
%0,8	5.84	2.68	24.89
%1,6	11.89	5.27	34.43

In conclusion;

- Single walled carbon nanotubes have their own electrical and photo physical properties. These features; when nanotube is doped in P3HT the P3HT is annihilated, which means it takes electrons from P3HT. Therefore, carbon nanotubes this ability to take electrons from P3HT shows that they can be used in organic solar cell production.
- SWCNTs create pellets when they are doped in P3HT because of Van der Waals interactions. These pellets break the surface morphology and decrease the open circuit voltage. As a result of this, efficiency is decreased. In order to prevent this decrease of efficiency, there occurs an efficient exciton separation. For that reason, the most proper solution is done by adding cyclohexanone in SWCNT doped P3HT.
- SWCNTs doping ratio increase in P3HT increases the Van der Waals interaction among carbon nanotubes. This situation increases the pellets concentration and efficiency is decreased. Because of that, the proper ratio to get the higher efficiency is determined by the experiments.
- Cyclohexanone dope P3HT:SWCNT:PCBM devices, carbon nanotubes create new charge carrier roads, and from the results got the short cut current is increased as 53% than the reference. The best efficiency is 2.24% at 0.2% SWCNT doped devices. This result shows that, the efficiency is healed 64% according to the reference.

5. REFERENCES

1. Aletli Analiz, Anadolu Üniversitesi Yayınları, Eskişehir, Eylül 2010.
2. Bernholc, Jerzy, Christopher Roland, and Boris I. Yakobson. "Nanotubes." *Current opinion in solid state and materials science* 2.6 (1997): 706-715.
3. Biercuk, M. J., et al. "Carbon nanotube composites for thermal management." *Applied Physics Letters* 80.15 (2002): 2767-2769.
4. Deniz A. Ergün, *Interfacial Layers For Improved Performance Of Small Molecule Bulk Heterojunction Organic Solar Cell*, Master thesis, Max Planck Ins. for Metal Research., Stuttgart, 2010.
5. Heidkamp, J. (2009). DIP growth on substrates relevant for organic solar cells. Non published PhD. thesis. Max Planck Institute of Metals Research in Stuttgart ve Institute of Theoretical and Applied Physics of the University Stuttgart.
6. Hoppe, Harald, and Niyazi Serdar Sariciftci. "Organic solar cells: An overview." *Journal of Materials Research* 19.07 (2004): 1924-1945.
7. [http://tr.wikipedia.org/wiki/Organik_Güneş_Pilleri_\(Hücreleri\)](http://tr.wikipedia.org/wiki/Organik_Güneş_Pilleri_(Hücreleri))
8. <http://www.nanoturkiye.net>
9. Keisuke Tajima, *Introduction to Organic Solar Cells*, 2008.
10. Liao, K.S; Yambem, S.D; Haldar, A; Alley, N.J; Curran, S.A (2010). *Designs and Architectures for the Next Generation of Organic Solar Cells.*, School of Physical Sciences, Dublin City University.
11. Lienerth, P. (2009). Electrical characterization of Organic semiconducting thin films. Non published PhD. thesis, Max Planck Institute for Metals Research in Stuttgart ve Institute of Theoretical and Applied Physics of the University Stuttgart.
12. Lu, Rongtao, et al. "Extraordinary Photocurrent Harvesting at Type-II Heterojunction Interfaces: Toward High Detectivity Carbon Nanotube Infrared Detectors." *Nano letters* 12.12 (2012): 6244-6249.
13. Melek B. Koç, *Nanotüpler, Lisans Tezi, Ankara Üniversitesi Müh. Fak. Fizik Müh.* 2003
14. Moliton, André, and Jean-Michel Nunzi. "How to model the behaviour of organic photovoltaic cells." *Polymer International* 55.6 (2006): 583-600.
15. Saito, Susumo, and Alex Zettl. *Carbon Nanotubes: Quantum Cylinders of Graphene: Quantum Cylinders of Graphene. Vol. 3. Access Online via Elsevier*, 2008.

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APENDIX



Spin coating on glass



Measurement in Glove box with precision scale



Drying the solvent in vacuum etuv



Preparing molecules used in the solvents

【評語】 100029

1. 有機太陽能電池的研究值得鼓勵。
2. 所使用的有機太陽能電池的結構，材料與製成符合一般的系統。
3. 使用單層奈米碳管有助於提升效率。
4. 建議針對參數調整優化的原理與機制作進一步討論。