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博 士 論 文

**Study on Carrier Dynamics of
p-n Heterojunction Organic Photovoltaic Cells
by Advanced Impedance Analysis**

先進インピーダンス分光解析によるp-nヘテロ接合型

有機薄膜太陽電池のキャリア挙動に関する研究

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Chapter 1

General Introduction

1.1. Motivation for photovoltaics

How to cope with the increasing energy demand is an important issue in the 21st century because in this century the population and economic will keep growing in the global-scale. Presently, we are facing the limited reserves of recoverable fossil fuel resources such as coal, petroleum and natural gas, which are accounting for more than 80% of global energy supply and carbon dioxide (CO₂) gas emission that is major contributor of the global warming.

The data presently available tells us that CO₂ concentration in air is increased from 280ppm (i.e., concentration before the Industrial Revolution) to 380ppm. It is predicted that due to the increase in greenhouse gas the global average air temperature will be increased by 1.4 to 5.8 deg.C at the end of the 21st century [1]. It is expected that this abrupt temperature rise would bring about such extensive damage as rise in sea water level, resultant loss of lands, increase of abnormal weather conditions like torrential rain and drought, adverse impacts on ecosystem, and progress of desertification. In order to sweep out negative factors like these global environmental issues caused by use of fossil

fuels, it is required to develop the new clean energy technology and to shake energy industries free from dependence on fossil fuels.

The clean energies can be obtained from hydroelectric power generation, tidal power generation, geothermal power generation, wind power generation, fuel cell power generation that uses natural gas and naphtha, bioenergy power generation that uses vegetation, and photovoltaic power generation or solar thermal power generation that use solar energy. Among these wide varieties of clean energies, the photovoltaic technology is expected to be the most prospective energy supply source for the mankind, and R&Ds of photovoltaic cells are being actively and progressively carried out.

The greatest benefit of using photovoltaic technologies around the world is that irradiation energy from the sun to the earth have a enormous energy ($8.5 \times 10^{16} \text{W}$). Furthermore, this solar energy exceeds the global consumption energy, $1.3 \times 10^{13} \text{ W}$. Therefore, to disseminate many photovoltaic technologies around the world, it has been required solar cells having higher performance and manufacturing in a low-cost way.

Indeed, the number of published paper about “photovoltaic cell” or “solar cell” has been increased significantly in each of the past ten years [2]. The number of published papers was a record high of over one thousand. In this context, it will be required the photovoltaic device having high power conversion efficiency (PCE) as energy source

which can supply electrical power covered the most of global consumption energy.

(Figure 1.1)

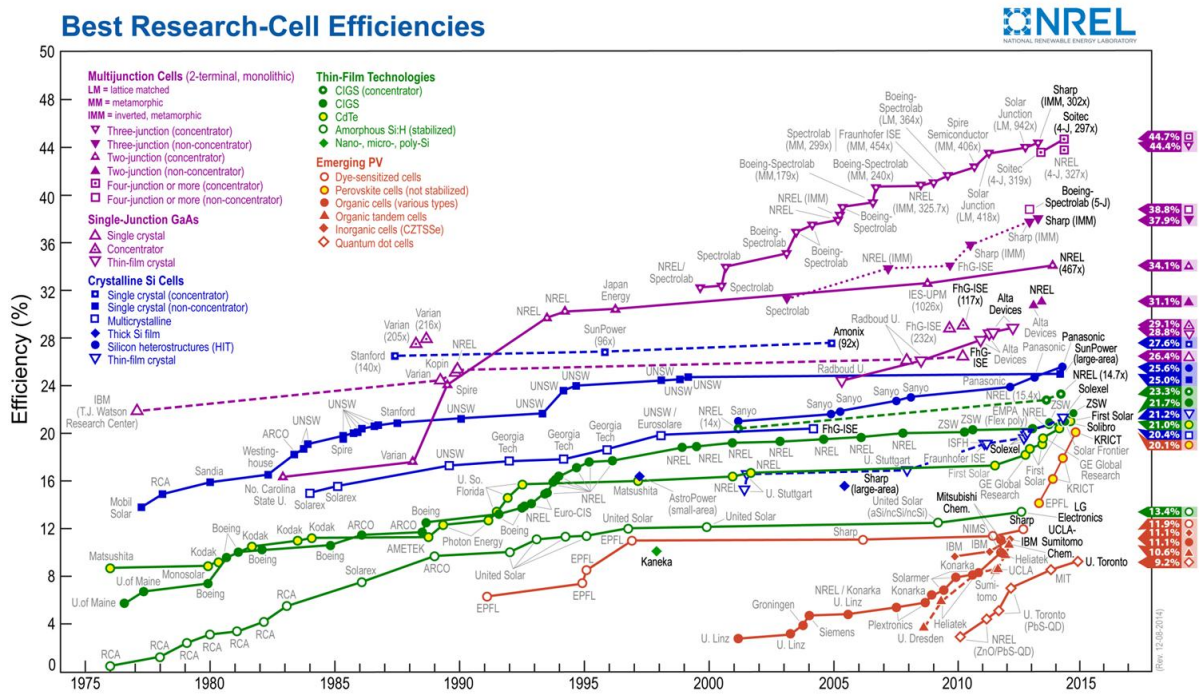


Figure 1.1 Research cell efficiency records plotted by National Center for Photovoltaics.

(NREL: <http://www.nrel.gov/ncpv/>)

1.2. Organic photovoltaics

—1.2.1. Advantages of organic photovoltaics

The bulk photovoltaic cells like crystal silicon cells are termed the first generation cells, and cells composed of thin film photovoltaic cells like a-Si and compound semiconductors are termed the second generation cells. As things stand now, there is not a common recognition about what types of cells should be termed the third generation cells. However, organic thin film photovoltaic cells have noted because of their features such as design flexibility, light weight, low price, and almost limitless available resource. In view of growing concerns about unstable resource availability of rare metals, which are cores of inorganic semiconductors whose prices are hiking recently, it would not be exaggeration to state that the ages of organic film photovoltaic cells will come in near future if it is acceptable to regard photovoltaic cells, only small parts of which are composed of organic materials, as organic film photovoltaic cells.

From these advantages, the OPVs have attracted much attention for application of great value products such as cell phone, car window, outside of house wall, greenhouse for agriculture accessory and so on. It will enable generation of electrical power everywhere and daylight. (Figure 1.2)

Until now, both of OPV device based on small molecules and polymer have been

developed. Many OPV devices based on polymer having high performance were reported. This reason is attributed to ease of fabricating device (e.g. spin-coat method).

On the other hand, OPV device based on small molecules have advantages although enable to fabricate using vacuum techniques is expensive. The highly-pure materials based on small molecules are available for OPV device due to high thermal stability. By use of the merit, it will be possible to realize OPV device having high performance and clarify the details of physical and/or chemical mechanism on removed impurities.

Organic light-emitting diodes (OLEDs) based on small molecules which emitted light by recombination of electrons and holes have already yielded practical applications such as display [3], interior illumination [4]. Organic electronics based on small molecule have a strong probability of success in future technology.

Direction of OPV development

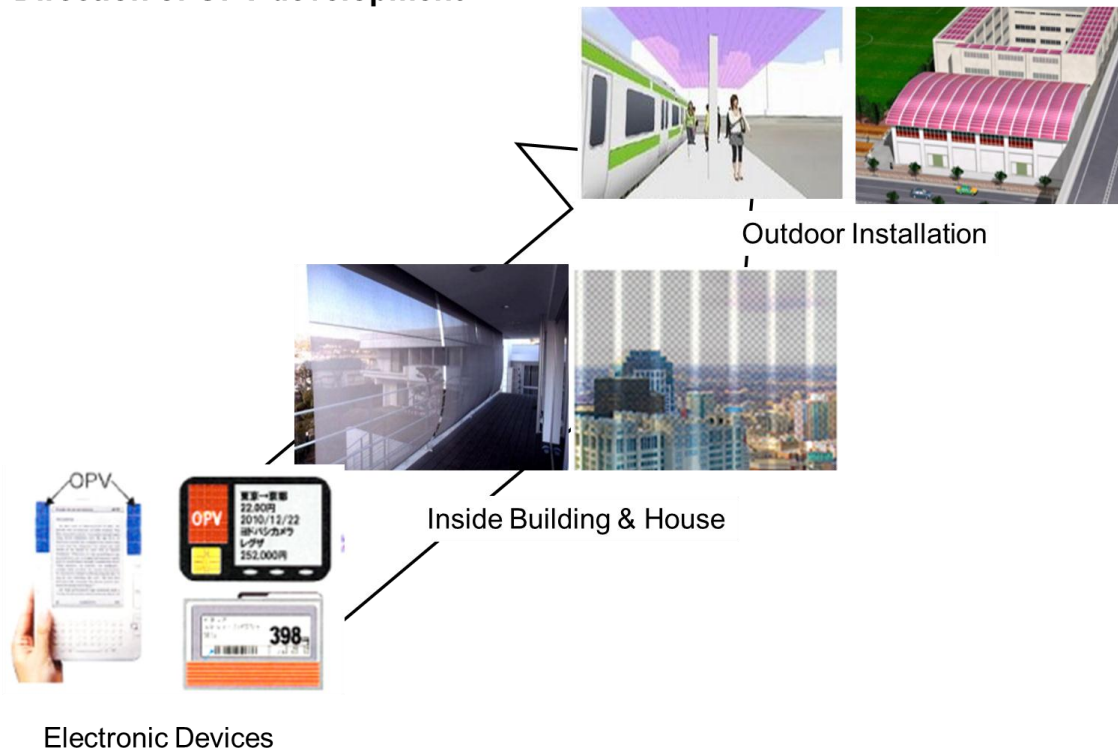


Figure 1.2 Direction of OPV development and application possibilities of the OPV devices.

—1.2.2. History of organic photovoltaics based on small molecules

In the first place, the best model of organic film photovoltaic cells is the photosynthetic system of vegetation existing in nature. Its high conversion efficiency indicates that the photosynthetic system of vegetation is the ultimate organic photoelectric converter. In recent years, various and intensive studies have been carried out to investigate these super highly efficient and ideal organic photoelectric converters, and some of them have been progressed as deep as molecular level analysis of antenna molecule and reaction center structures in photosynthetic system [5]. Before introducing various types of organic film photovoltaic cells, the history of past studies are described in the rest of this sub-section.

The history of organic film photovoltaic cell study is very old [6], and if we define that the study has begun with the discovery of photoconductivity in organic material, we could say that the history began in about 1900. It required almost a half century since that discovery to start investigating organic materials by applying the concept of photovoltaic power to the materials, which indicates how it had been difficult to try to apply organic materials to photoelectric converter in those years. However, over these last 20 years, the conversion efficiency of organic film photovoltaic cells has been improved more rapidly than those of any other types of photovoltaic cells. This rapid

improvement of the efficiency is attributable to the long history of studies from 1970s to the present, but when we discuss the history, it is indispensable to introduce two big breakthroughs. One of the breakthroughs is a formation of organic heterojunction photovoltaic cells made by Tang [7], and another breakthrough is a formation of bulk heterojunction photovoltaic cells made by Yu and others [8].

In the history of organic film photovoltaic cell development described in this section, the structure of photovoltaic cells before the breakthroughs and that of two breakthroughs are summarized. (Figure 1.3)

[Schottky barrier junction photovoltaic cell]

The organic film photoelectric converters in their early days were those of the Schottky type, in which organic dye was sandwiched with electrodes. It made use of exciton's electric charge separation with the Schottky barrier junction electric field that was formed on the interface between p-type semiconductor and electrodes. Between 1970s and 1980s, single layer cells, in which a variety of p-type semiconductors were used, were intensively studied [9]. The energy conversion efficiency in these studies was limited to 0.7% in the case where Merocyanine film cells were used [10], and the efficiency had not exceeded 1%. This may be mainly because that, due to exciton

binding energy of organic molecules that is stronger than that of inorganic molecules [11], the electric charge separation in organic molecules cannot be done efficiently at the interfacial bonding electric field.

[Heterojunction photovoltaic cell]

In 1986, Tang reported that he achieved the conversion efficiency of 0.95% in the organic heterojunction photovoltaic cell composed of the lamination of copper phthalocyanine and perylene derivatives [7]. This conversion efficiency of nearly 1% is the first in the history and this event can be regarded as the first breakthrough. There are three reasons why the efficiency of organic heterojunction cell can be increased better than that of organic single layer cell.

Tang's achievement triggered and activated the studies focusing on the p-n heterojunction cells. In 1990s, cells composed of various metal phthalocyanine and perylene derivatives were studied, but the conversion efficiency that Tang had achieved could not be obtained. New approaches, in which various cells are layered structure, have been studied for the further improvement of efficiency. For example, P. Peumans and al reported in 2000 that cells in which exciton blocking layer was used to avoid exciton deactivation caused by surface plasmon at organic film/metal interface [12]. Also in

2001 cells having tandem-type photoelectric conversion structure was reported [13]. As a result of efforts to improve cell performance in term of materials, it is reported that conversion efficiency of 3.4% was obtained with the cells in which n-type fullerene was used [14]. The target of the following studies has shifted to the investigation of the bulk heterojunction structure, and the competitive studies to increase the efficiency in pure heterojunction cell structure subsided. However, the heterojunction structure composed of a variety of films is suitable for clarifying the physical principle of organic film photoelectric conversion, and it can be said that the heterojunction cell played a very important role in the history.

[Bulk heterojunction cell]

The heterojunction photovoltaic cell had a large obstacle impeding the efficiency enhancement, in that, due to short exciton diffusion length in organic materials, only the lights absorbed in the region very proximate to organic/organic interfaces can contribute to the photovoltaic current generation.

To remove this obstacle, an improvement in term of structure was made, resulting in the bulk heterojunction structure that can be regarded as another breakthrough. In the bulk heterojunction structure, donor (D) and receptor (A) molecules are mixed or combined

alternatively, and the D/A heterojunction interfaces, in which electric charges are separated, are distributed over the entire light absorption layers. Thanks to this wide distribution of the light absorption layers, the distance for excitons to reach the D/A heterojunction interfaces can be shortened, and excitons can be converted highly efficiently to free carriers over the entire absorption layers. In other words, when a planar heterojunction cell becomes thicker the conversion efficiency is restricted by the exciton diffusion length but in the case of bulk heterojunction cell it becomes possible to improve both of solar absorptance and carrier generation efficiencies at the same time regardless of cell thickness.

On the other hand, electrons and positive holes may be sometimes recombined in some of bulk heterojunction layers, reducing free carrier extraction efficiency to each electrode. In the heterojunction structure, donor receptor molecules exist continuously to each electrode, however the bulk heterojunction layer does not such structure as heterojunction structure and thus it does not have the chemical potential caused by concentration gradient of free carriers that are created in the interface. Also in the bulk heterojunction layer has a lot of discontinuous phases and the interface between continuous and discontinuous phases may trap carriers. These two natures (i.e., lack of chemical potential and carrier trap) of bulk heterojunction structure are reasons why free

carrier extraction efficiency is reduced. In other words, it is a key for higher conversion efficiency in the bulk heterojunction cells to form smooth carrier transfer path so that the carrier extraction efficiency can be improved.

In 1995, Yu et al., reported the bulk heterojunction structure whose efficiency exceeded the preceding efficiencies at a breath. In their approach, high molecules and fullerene molecules were blended in the structure. Application of high molecular materials to the photoelectric converter is detailed in next section.

Also in the structure using low molecule materials, the concept of the bulk heterojunction structure has been implemented by introducing the co-deposition of donor and receptor molecules with the vacuum deposition method [15]. Nanostructure control of co-deposition layer formed with donor and receptor molecules [16] and bulk heterojunction structure called "p-i-n" structure have been applied in the heterojunction cell [17, 18]. In 2005, Forrest et al. reported the conversion efficiency of 5.7%, which is the best efficiency even as of today in the organic thin film photovoltaic cells [19]. They were focused their design to light absorption exciton diffusion length and could achieve this efficiency based on the detail design that was a culmination of knowledge and findings obtained so far.

Cell structure of OPV

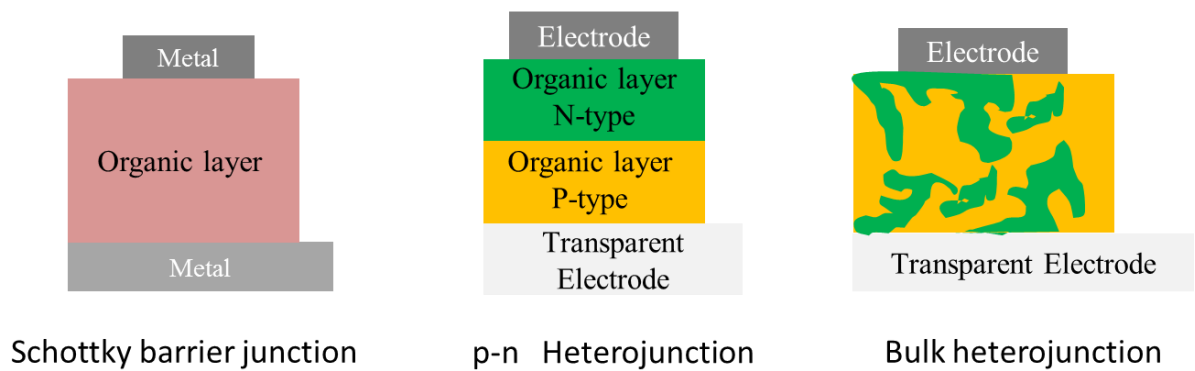


Figure 1.3 Structure of organic photovoltaic (OPV) cells.

1.3. The importance of carrier dynamics study

— 1.3.1. Performance of organic photovoltaics

In order to investigate the performance of organic photovoltaic device, the measurement of current density-voltage (J-V) characteristics in the dark and under illumination was needed. Figure 1.4 shows a J-V curve of a photovoltaic device in the dark (blue line) and under illumination (yellow line). When the device is illuminated, the J-V curve is shifted down by the amount of photocurrent generated. The open-circuit voltage (V_{OC}) defined as voltage at $J=0$. The maximum current that can run through the cell at $V=0$ is called the short-circuit current, J_{SC} . The maximum of the obtained electrical power (P_{max}) is located in the product of current density J and voltage V reached its maximum value ($J_{max} \times V_{max}$; see Figure 1.4). The ratio between P_{max} and the product of J_{SC} and V_{OC} measures the quality of the shape of the J-V characteristics, and defined as the fill factor (FF). Thus, FF is expressed by as follows.

$$FF = \frac{J_{SC} \times V_{OC}}{P_{max}} \quad (1.1)$$

thus $P_{max} = J_{SC} \cdot V_{OC} \cdot FF$. The power conversion efficiency (PCE) of a device is the ratio between the maximum output power P_{max} and the power of the incident light (P_{in}):

$$PCE = \frac{P_{\max}}{P_{in}} \times 100 = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \times 100 \quad (1.2)$$

Because $P_{\max}$ depends on the wavelength and intensity of the incident light, the PCE should be measured under standard test conditions. Usually, the equation (1.2) was normalized by simulated sunlight, that is, light spectra of Air Mass 1.5G (AM1.5G), intensity of 100 mW/cm^2 . Normalized PCE is indicated by the following equation.

$$PCE = J_{sc} \times V_{oc} \times FF \quad (1.3)$$

In order to increase PCE, for the same incident light power, all of J_{sc} , V_{oc} , and FF need to be increased. In organic photovoltaic device based on bulk heterojunction, these values strongly depend on fabricated condition and measurement environment such as: thickness of active layer [20], light intensity [21], temperature [22], with or without organic/metal interfacial buffer layer [23-25] and so on.

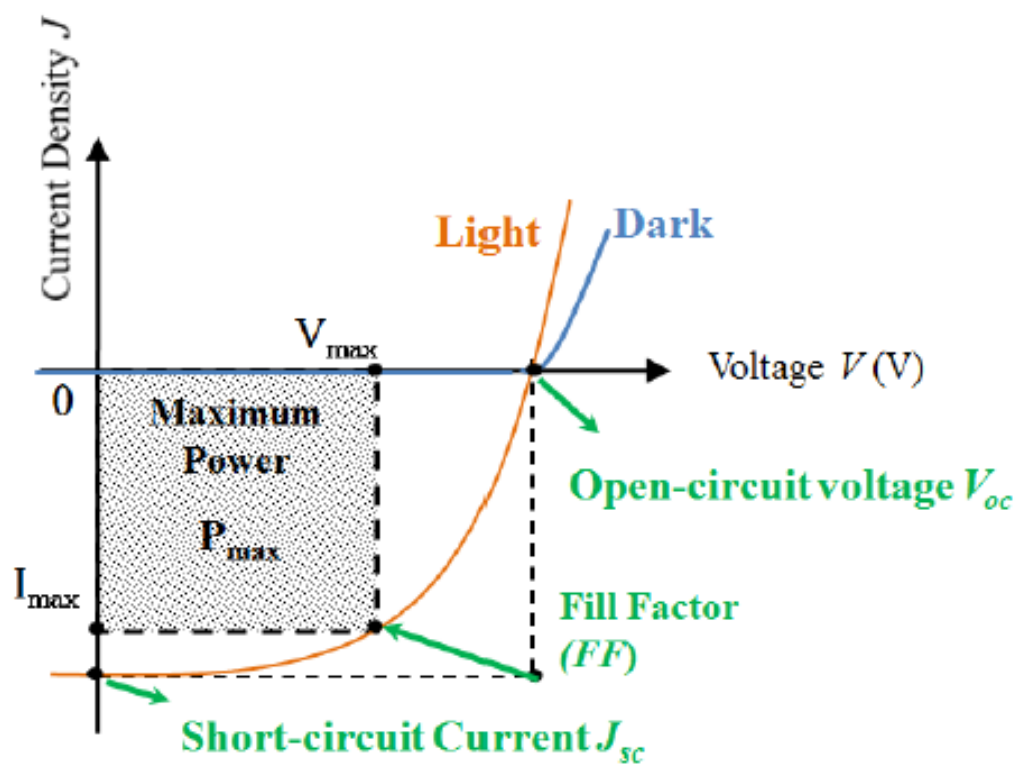


Figure 1.4 J-V characteristics of an organic photovoltaic device in the dark (blue line) and illumination (yellow line) conditions.

— 1.3.2. Principle of p-n heterojunction structure

The origin behind a heterojunction is to bring together two materials with different ionization potentials and electron affinities. As described above, the PCE of Prof. Tang's reported planar-type cell is higher than that of schottky-type cell. This result means that the presence of interface area between donor and acceptor must be generating many free charge carriers. Prof. Tang proposed that the observed synergistic effect of bringing two different semiconductors in contact was caused by the field at the heterojunction interface. This local field aids dissociation of excitons diffusing to the interface. "Exciton" defined as electron-hole pair bounded by coulombic interaction.

The energy diagram is shown in Figure 1.5. The 4 steps of photocurrent generation in OPV are as follows:

- (1) Photons which absorbed inside device excite electrons from HOMO to LUMO level.
(that is, generation of excitons).
- (2) Excitons start to diffuse in organic films
- (3) Excitons reached at donor-acceptor interface are dissociation. (leading to charge separation)
- (4) Charge carriers are transported to electrodes (carrier collections at electrodes)

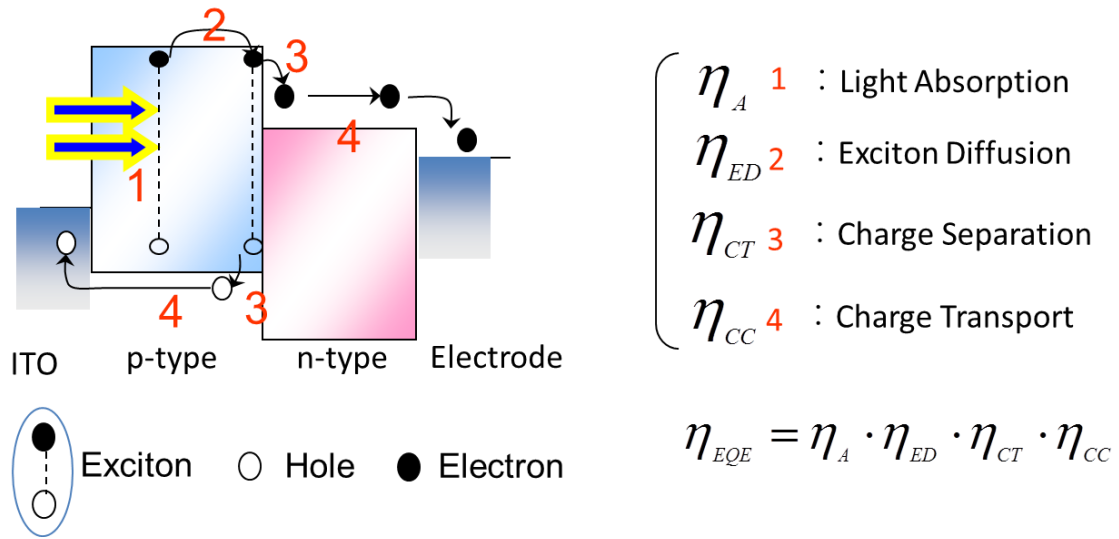


Figure 1.5 The 4 steps of photocurrent generation in OPV.

— 1.3.3. Importance of p-n heterojunction structure

It will not be too much to say that, thanks to the invention of bulk heterojunction structure, conversion efficiency has been increased even in the single layer cells, and that the way to commercialization of organic thin film photovoltaic cells has been opened. The efficiency has been kept increasing year by year but it seems that the theoretical understanding of the phenomenon cannot keep pace with the increasing efficiency. When we take the further enhancement of the efficiency into considerations, knowledge and findings thus far accumulated about layered structure should be very instrumental to theoretically investigate the power generation in the organic film photovoltaic cells.

One of features of heterojunction cells is that each film layer is composed of one organic semiconductor material, and thus it is also important to evaluate the cell performance and characteristics of each film layer. In other words, by making use of merits inherent to organic materials that they can be designed to have arbitrary molecular elements, each layer can be studied systematically with the proper design of the layer.

In the small molecules whose films are formed with the vacuum deposition method, the multilayer construction technique has been utilized as a matter of course. That is, in

making the heterojunction cell the performance required in each layer such as light absorption wave band, carrier transport capability, and energy level shall be defined in the first place. Since it is possible to study correlation between cell characteristics and required performance, the heterojunction cell has the structure suitable for physical investigation of the performance.

It is indispensable to develop new materials that are excellent in their exciton transport and electric charge separation functions in order to further improve the conversion efficiency of organic film photovoltaic cells. To support the development, it is essential to study the basics aspect of the materials and to deepen the knowledge about them. To meet these requirements, it is important to investigate the layered structure of organic photovoltaic cells by impedance spectroscopy method.

1.4. Impedance spectroscopy

In the Impedance Spectroscopy method, DC voltage superimposed by small sinusoidal wave voltage signals is applied to a cell to measure impedance of the cell [26]. The spectrum of the impedance can be analyzed by sweeping AC signal modulation frequency widely from low to high frequencies. As discussed in the previous section, the organic film photovoltaic cell is the composite laminate of organic semiconductor films, each of which has different optical and electronic properties.

With the IS method, the impedance of the organic semiconductor layer and that of interface layer between electrode and semiconductor can be measured separately from others, making it possible to decide the equivalent circuit that expresses semiconductor and interface layers in the organic electronic cells with such circuit characteristics as resistance and electrostatic capacity. By investigating changes in equivalent circuit constants and in shape of equivalent circuit with operation time, it is possible to investigate where carriers are accumulated and transported in the cell and how photoconductivity changes continuously and non-destructively. The IS measurements have been carried out and reported regarding organic electronic cells such as organic EL cells [27 - 33], organic MIS (Metal-Insulator-Semiconductors) cells [34], and organic solar cells [35 - 39], and the equivalent circuit for these cells have been experimentally

decided.

As described in the preceding section, power is generated in organic film photovoltaic cell cells when electrons and positive holes are discharged to the external circuit after being subjected to such process as exciton generation by light illumination, electric charge separation into free carrier at donor/receptor interface, carrier transportation within each layer, and accumulation of carriers in the interface. Since a lot of photo/electronic processes can be observed with the IS method, impedance spectrum can be monitored as a function of applied voltage signal frequency, which allow the multiple operation processes having variety of time constant to be separated. With this separation, it becomes possible to decide changes in electro conductivity and physical property like carrier mobility in each film layer that forms laminated organic film photovoltaic cell. These measurements of physical properties that will decide the performance of organic film photovoltaic cell cells are effective in clarifying operation principle and power generation mechanism, and at the same time they will provide important guideline to enhance performance of organic film photovoltaic cell.

In impedance spectroscopy, an analysis is performed using two transfer functions: impedance Z of the resistance component and modulus M of the capacity component. Z has been commonly used as a transfer function in the analysis as it can effectively

analyze diode characteristics of a voltage region where the resistance drastically changes when a large amount of charge is injected due to application of voltage.

On the other hand, the organic solar cell used in this study is a device with a thin film that does not originally have free carriers. The dynamics of carriers, such as the behavior of charge storage in the interface of the p-n junction of the device and the conduction of photo carriers when a very small amount of light is irradiated, have to be determined by applying a small amount of voltage and slightly changing the resistance component. (Figure 1.6) Therefore, establishing an advanced analysis of impedance in place of the conventional analysis of the impedance Z is desired.

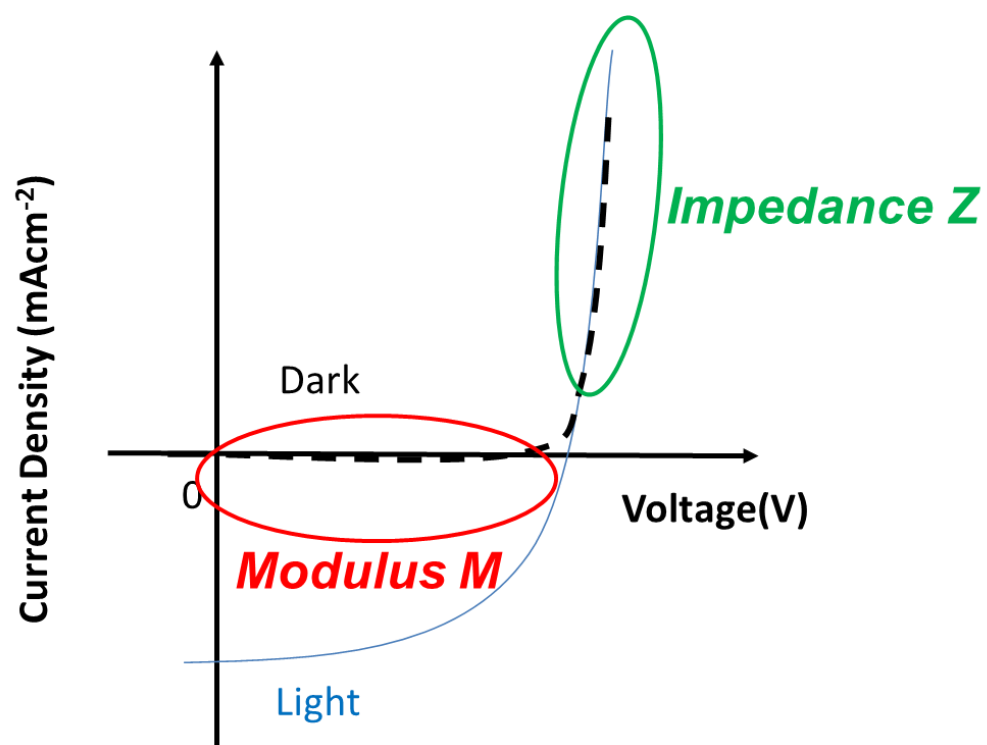


Figure 1.6 Suitable region of the analysis by using Modulus plots in the case of OPV.

1.5. Objection and outline of this thesis

In this study, we consider that the analysis of modulus is effective in detecting the behavior of a very small amount of charge by focusing a transfer function of the modulus M of the capacity component, and we try to apply it as an advanced analysis of impedance for the dynamics of carriers of the organic thin-film solar cell.

The objectives of this study are to establish the advanced analysis of impedance by using a transfer function of M and to demonstrate the effectiveness of the analysis.

The effectiveness of the analysis of modulus was verified when it was effectively used to analyze the following two types of behaviors of a carrier. First, to clarify differences of the behavior according to the thickness and the organic semiconductor materials, the behavior of charge storage in the interface of the p-n junction was analyzed using an actual organic thin-film solar cell under a dark environment where light is not radiated. Second, the possibility of directly measuring the conductivity of an optical carrier in each p and n layer was shown during light irradiation similar to when the solar cell is operated.

By showing the applicability and effectiveness of the advance analysis of impedance in each of the two operation conditions of the organic thin-film solar cell, we prove that this analysis method is effective in analyzing the dynamics of a carrier in the organic

thin-film solar cell.

As described in previous sections, it is important to clarify carrier movement mechanism within the cell in order to further enhance the conversion efficiency of organic film photovoltaic cell. The IS measurement has received large attention in recent years but there are a few examples that the IS measurement has been applied to organic film photovoltaic cell, and the discussion about physical properties and equivalent circuit shape that can be decided with the IS measurement has just started. In this study, we tried to clarify carrier dynamics of typical laminated organic film photovoltaic cell with the IS analysis.

In Chapter 2 "Experimental", the principle of vacuum deposition method is described because this method is mainly used to manufacture the laminated organic film photovoltaic cells used in this study. The experiments in this study are also detailed in Chapter 2. Also described in this Chapter are the impedance measurement methods and various transfer functions used in the analyses.

In Chapter 3 "Carrier Dynamics of p-n Heterojunction Organic Photovoltaic Cells Analyzed by a Novel Graphical Representation of Impedance Spectroscopy", modulus plot focusing on the capacitance component of the transfer function is used to analyze organic film photovoltaic cell. Externally applied voltage and film thickness are varied

and their modulus are analyzed in order to clarify the existence of internal electric field that induces carrier accumulation, which lowers energy conversion efficiency at interface between film layers composed of p and n type organic semiconductors. Also new p type semiconductor material has been developed and it is clarified that, based on the modulus analysis of this new semiconductor material, the internal electric field is weakened and cell characteristics have been enhanced.

In Chapter 4 "In-situ Measurement of Photoconductivity of Multilayered Organic Photovoltaic Cells by Impedance Spectroscopy", carrier photoconductivity that is induced by illuminating light on each layer of the laminated organic film photovoltaic cell is directly measured. Frequency characteristics analyzed while varying the intensity of illuminated light verified that two components having different relaxation time were separated, and it was identified that they were caused by changes in photoconductivity of carriers induced by lights illuminated in each film layer. Also it is experimentally verified with the actual organic film photovoltaic cells that photoconductivity and carrier mobility could be calculated.

In Chapter5 "Conclusion", the studies in Chapters 3 and 4 are summarized, and at the same time the factors promoting the higher energy conversion efficiency are described from the stand point of carrier behavior analysis that is carried out to enhance organic

film photovoltaic cell performance. In addition, the guideline of R&D for the betterment of the performance is proposed.

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Chapter 2

Experimental

2.1. Impedance spectroscopy

—2.1.1. Measurement method

The IS method has a wide variety of applications, and it has been mainly applied in the electrochemical measurement [1]. As described in the above Sections, the IS method is also very effective method to measure the organic electronic cells but it has a short history of applications to the actual cells. It is awkward to say that the measurement method, analysis method, and theory that can fully explain/interpret the measurements have been established. Thus, conditions and procedures in the IS method applied to the measurements of organic film photovoltaic cells are described in detail in this section. The method described in the following sections is believed that it is generally applicable to organic film photovoltaic cell, and except for some exceptions, the measurements described in this paper are carried out in line with this general method.

—2.1.2 Measurement theory

In the IS method, very small sinusoidal wave voltage signal [$V = V_1 \exp(i\omega t)$] is applied on an electronic cell, and current amplitude of response current signal $\{I = I_1 \exp[i(\omega t + \phi)]\}$ is measured. Impedance [$Z = V/I = V_1/I_1 \exp(-i\phi)$] of the cell is obtained based on the phase difference between the current amplitude and input signal (Figure 2.1) [2]. For example, an electronic process that has long relaxation time cannot follow the change of electric field when high frequency voltage is applied to an cell, and thus only the impedance of the process that has short relaxation time can be measured. As the frequency of applied voltage decreases, the electronic process that has longer relaxation time will become able to follow the change of electric field, and thus the impedance of the process that has long relaxation time will be able to be measured. Therefore, it is possible to measure the impedance of the process having particular relaxation time separately from that of other processes.

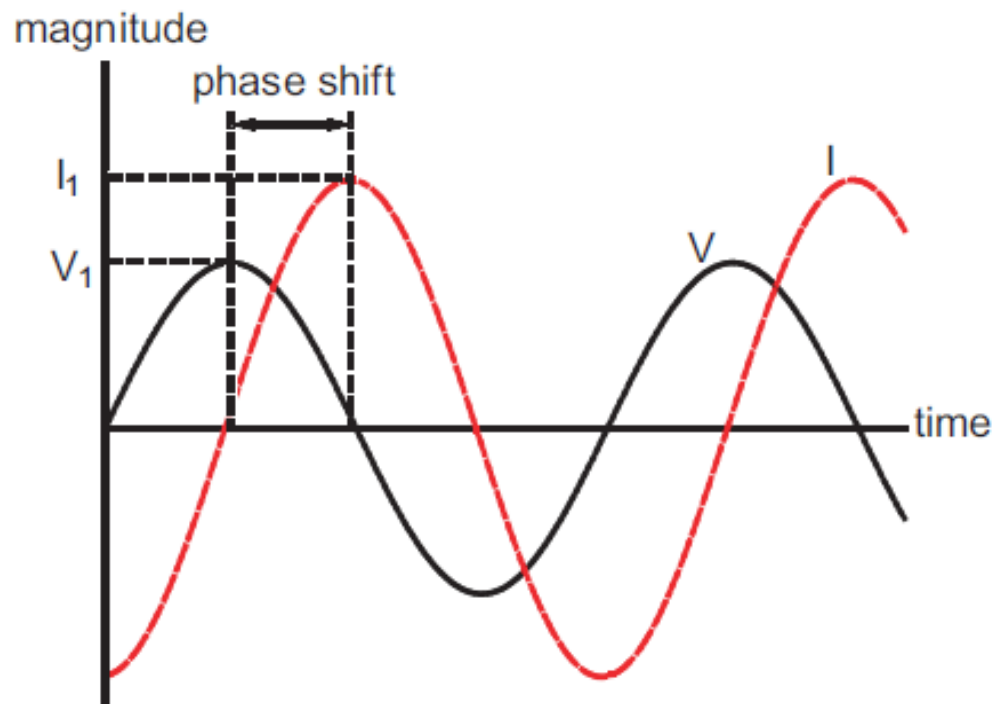


Figure 2.1 A sine wave voltage generating input signal and a response current signal curve.

—2.1.3 Measurement equipment

The IS measurement can be carried out only with a function generator and lock-in amplifier, which outputs the input signal to an element and measures amplitude and phase of output signal, respectively. However, in order to accurately measure signals in wide range of frequency, it is desirable to use a Frequency Response Analyzer (FRA). The FRA has a superior noise removal function, and can analyze the response only from the frequency component you want to investigate. It also has a frequency automatic sweep function to simplify the IS measurement. In this study, we used Hewlett-Packard's FRA (Impedance analyzer: HA4294A: Figure 2.2).



Figure 2.2 Hewlett-Packard's FRA (Impedance analyzer: HA4294A).

—2.1.4 Measurement conditions

Especially when the FRA is used in the measurement, there is a potential risk to make the measurement under improper condition because the FRA is easy to operate. The measurements in this study were made under the following conditions and settings:

1. Very small AC signal

Check if conditions for the very small AC signal are met. Measure impedance while varying the applied AC voltage between 10 mV and 200 mV, and check that the impedance does not change with the magnitude of the applied AC voltage. Under the very noisy conditions, S/N ratio is improved by increasing AC voltage but the ratio shall not be different from the ratio when small AC voltage is applied.

2. Frequency zone setup

As a matter of course, the wider the frequency zone is, the more various components can be measured. However it is required at least one cycle of the signal to lock on the response current signal and to make meaningful measurement. Thus when the measurement range is expanded toward the lower frequency side, it takes extremely longer period of time to make the measurement. When measuring such cell as organic film photovoltaic cell whose performance could vary during the measurement, it is recommended that the measurement should be started from the high frequency side.

3. Integration cycle (time) setup

Since FRA has excellent noise removal performance, normally one cycle of the measurement is good enough to get meaningful measurement. However, the output from FRA may sometimes be largely different from the correct output when the waveform is deformed by noises and other factors because FRA uses its specific algorithm to calculate the output. Especially in the low frequency zone the S/N ratio could go wrong and thus it is necessary to make measurement for two or more cycles if the ratio is not good. Note that the larger the number of cycles the longer the time required for the measurement is.

4. Measurement in high frequency zone

In high frequency zone, there are such phenomena as signal attenuation in the cable connecting between FRA and measured cell and reflection of a part of signals from the cell. These phenomena could deform the wave form and phase could not be detected correctly, resulting in incorrect measurement. The incorrect measurement could be avoided by connecting FRA directly to the measured cell or if this direct connection is not feasible the cable length should be shortened as short as possible. Or influence from the measurement circuit can be removed by making use of the data measured when the cell is not connected yet, and this removal of the influence can be done with the internal

reverence function of FRA. However the time required for completing the measurement is doubled. When the measurement range is expanded toward higher frequency zone, the higher carrier mobility can be measured.

After confirming the above conditions and restrictions, the measurement conditions of this study are determined as follows: AC voltage superimposed on the DC voltage is from 30 mV to 100 mV. Frequency of AC voltage is between 100 Hz to 1 MHz and the frequency is swept from high to low frequency. Integration cycle (time) is one second for the frequency zone of 100 Hz or more and the measurement is repeated twice when the S/N ratio is low. The measurement is made in the atmospheric environment and at room temperature. The measurement is made in the aluminum box that is grounded in order to reduce noises and to make in the dark.

2.2. Analysis

Not only it is awkward to say that the measurement method has been established, but so analysis method is. Analysis only on the complex impedance plane cannot give all the information contained in the impedance. The FRA can provide a lot of data with ease but the interpretation of the data sometimes comes to an impasse because how to analyze the data is not known.

—2.2.1 Analysis with Cole-Cole plot

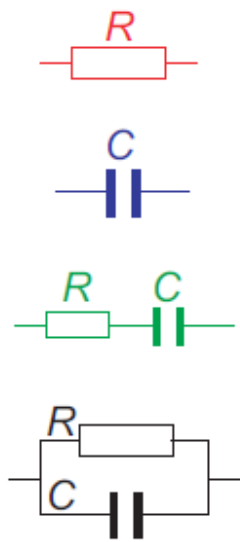
Plot of impedance measured at various applied voltage signal (i.e., at various parameters) on the complex plane is termed Cole-Cole plot. The basic transfer functions such as modulus, admittance, and conductivity can be derived from the impedance [2]. The transfer function suitable for the purpose of the analysis can be from these four transfer functions. In this study, transfer functions of impedance (Z) plot and modulus (M) plot are selected. The Z plot indicates resistance component of the impedance on the real axis, and M plot indicates the inverse of capacitive complement of the impedance.

The Z and M plots shall be analyzed at the same time in order to analyze the entire frequency zone (from low to high frequency) in detail. For example, when two components have similar time constant in the high frequency zone, it is difficult to

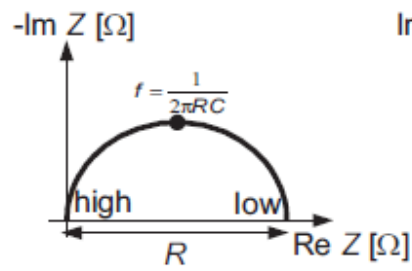
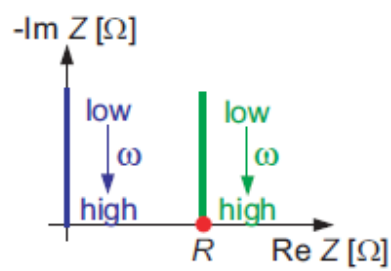
analyze the impedance in detail on the Z plot. However on the M plot the impedance is multiplied by the factor of $i\omega$, which allows the impedance to be investigated in detail in the high frequency zone.

In analysis with the IS method, an equivalent circuit of the cell is estimated from the impedance trace in the Cole-Cole plot. It is general practice to adjust and finalize the equivalent circuit by aligning the impedance trace in the Cole-Cole plot calculated by the estimated equivalent circuit to the Cole-Cole plot of measurement data. Figure 2.3 shows Z and M plots of typical circuit elements.

Equivalent circuit



Z plot



M plot

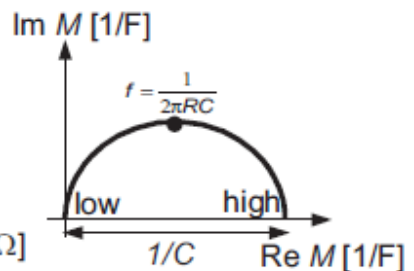
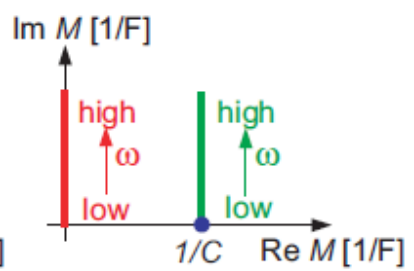


Figure 2.3 Typical equivalent circuit elements and Cole-Cole plots of Z and M plots.

The impedance trace of each circuit element has the following nature:

- Resistance (R)

(Z plot)

Since Z is equal to R ($Z = R$), impedance is shown with point R on the real axis.

(M plot)

Since M is equal to $i\omega R$ ($M = i\omega R$), impedance is shown with linear line on the imaginary axis and converges onto the origin at low frequency.

- Capacitance C

(Z plot)

Since Z is equal to $-i/(\omega C)$ ($Z = -i/(\omega C)$), impedance is shown with linear line on the imaginary axis and converges onto the origin at high frequency.

(M plot)

Since M is equal to $1/C$ ($M = 1/C$), impedance is shown with point 1 ($=C$) on the real axis.

- When a circuit is "R-C series circuit";

(Z plot)

Since Z is equal to " $R - i/(\omega C)$ " ($Z = R - i/(\omega C)$), impedance is shown with linear line parallel to the imaginary axis and converges onto the point R on the real axis at high frequency.

(M plot)

Since M is equal to " $1/C + i\omega R$ " ($M = 1/C + i\omega R$), impedance is shown with linear line parallel to the imaginary axis and converges onto the point $1/C$ on the real axis at low frequency.

- When a circuit is "R-C parallel circuit";

(Z plot)

Impedance is expressed with the following equation:

$$Z = \frac{R}{1 + \omega^2 R^2 C^2} - i \frac{\omega R^2 C}{1 + \omega^2 R^2 C^2} \quad (2.1)$$

The above equation is expressed in the next form when ω in the above equation is eliminated:

$$\left(\text{Re } Z - \frac{R}{2} \right)^2 + \text{Im } Z^2 = \left(\frac{R}{2} \right)^2 \quad (2.2)$$

This equation shows a plot of semicircle whose center is in the high frequency side, and whose diameter is equivalent to R.

(M plot)

Modulus is expressed with the following equation:

$$M = \frac{\omega^2 R^2 C}{1 + \omega^2 R^2 C^2} + i \frac{\omega R}{1 + \omega^2 R^2 C^2} \quad (2.3)$$

The above equation is expressed in the next form when ω in the above equation is eliminated:

$$\left(\operatorname{Re} M - \frac{1}{2C} \right)^2 + \operatorname{Im} M^2 = \left(\frac{1}{2C} \right)^2 \quad (2.4)$$

This equation shows a plot of semicircle whose center is in the low frequency side, and whose diameter is equivalent to the inverse of C.

—2.2.2 Analysis with frequency characteristics

In the analysis with Cole-Cole plot, frequency is a parameter of each plot, and it is hard to know the time constant of each component. In order to know the changes of time constant for carrier transport elementary process (e.g., carrier transit and acquisition of/emission from localized level), it is necessary plot the capacitance, conductance, and dielectric loss factor (in vertical axis) as a function of frequency (in horizontal axis). The details of changes in the time constant will be discussed in the later section. Dependency of imaginary part of the modulus on frequency is instrumental to investigate changes in the time constant at each component.

—2.2.3 Analysis of Dynamic Modulus Plot (DMP)

In general, electronic devices are represented by a combination of capacitance and resistance components in response to an external field. Carrier density and electron levels are evaluated based on C-V and f-C measurements in semiconductor engineering. In the electrochemical field, Cole–Cole plots, which are a representation of the impedance spectrum, have been used frequently [3]. The equivalent circuits of p-n heterostructured OPV, which separates specific functionalities to discrete layers, are complex components of each element. It is necessary to separate and analyze the individual responses of the components. Therefore, Cole–Cole plots are used to perform the separation and analysis using the difference in the frequency response of each element. By plotting the complex modulus data on a complex plane, we obtain an impedance Cole–Cole plot. In conventional p-n junction theory, negative bias voltage places the carrier away from the junction. This depleted region works as a capacitor, which is connected to the conductive region. Therefore, the equivalent circuit is a series connection of a resistor and a capacitor. However, organic materials have very few free carriers so that they are not semiconductor but dielectrics. Therefore, organic layers are well represented by equivalent circuits of capacitance resistance (CR) parallel circuits. The impedance (Z) of an organic layer is described by Eq. 2.5.

$$Z(\omega) = \frac{R}{1 + j\omega CR} \quad (2.5)$$

$Z(\omega)$ becomes a semicircle in the Cole–Cole plot, which is the Nyquist plot of imaginary Z vs real Z . The radius of this impedance Cole–Cole plot corresponds to the resistance of the layer. The impedance of the layered devices is described as the sum of Eq. 2.5. The impedance representation can be translated to the capacitance representation, which is called the modulus (M), defined by:

$$M(\omega) = j\omega Z(\omega) \quad (2.6)$$

When an arc appears in the impedance Cole–Cole plot, a corresponding arc appears in the modulus Cole–Cole plot. Its diameter is the reciprocal value of capacitance (C) (Figure 2.4). Because the dielectric constants are mostly 3.0 in many organic materials, the diameter of the arc rescaled by the surface area (S) in the modulus representation represents the effective thickness of the film. The semicircle means that carriers accumulate in the dielectric regions which become conductive. The stacked layers are represented by a series connection of these CR parallel equivalent circuits. The value of

the x-coordinate component in the modulus Cole–Cole plot becomes the effective thickness by rewriting the real part of the modulus as $d = \epsilon \epsilon_0 S \operatorname{Re} M(\omega)$. It is easy to identify which arc corresponds to which layer by observing the correspondence between the effective film thickness, estimated from the capacity, and the planned film thickness.

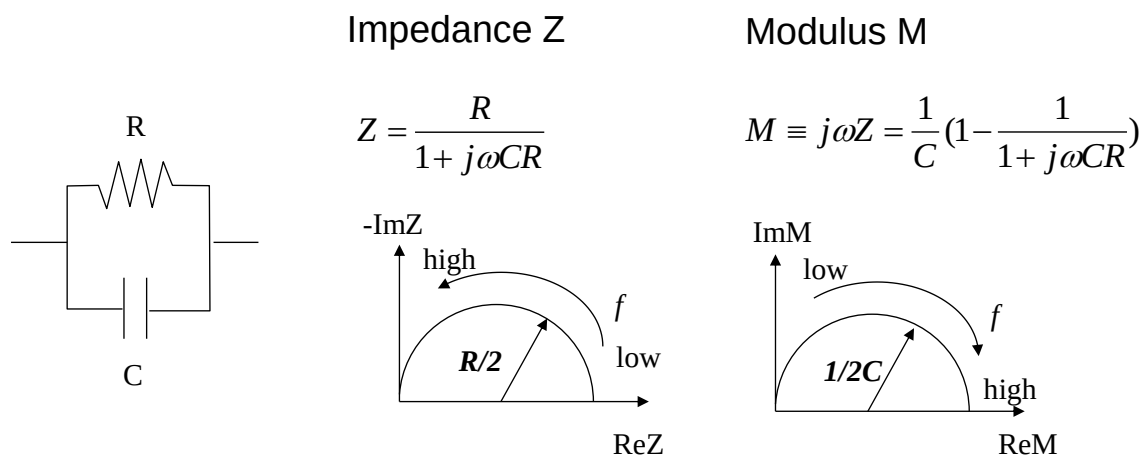


Figure 2.4 Cole–Cole plots of impedance (Z) and modulus (M). An organic layer is represented by an equivalent circuit of a resistor and capacitor connected in parallel. A circle is observed in both Z and M Cole–Cole plots. The radius of the circle in the Z and M Cole–Cole plots are the value of resistance and capacitance, respectively.

Here we propose a new graphical representation for the voltage-current response function, the dynamic modulus plot (DMP). The DMP is a compilation of the modulus plots obtained by frequency sweep, which are measured under various bias voltage conditions. The frequency sweep of the current response to the small AC modulation voltage is recorded for various DC bias voltages. The data obtained from the frequency sweep are converted to complex modulus data. By plotting the complex modulus data on a complex plane, we obtain a modulus Cole–Cole plot. The modulus Cole–Cole plots for various bias voltages are re-plotted so their imaginary parts are offset by the bias voltage, and the imaginary parts are rescaled by arbitrary values. Usually, the semicircles of organic electronic devices in the Cole–Cole plots are expressed by precise circles such that the lack of the scale of the imaginary part does not cause any confusion. We call this compilation of the modulus plots the DMP. Here, we note that the envelope at the lowest frequency points is the Mott–Schottky plot.

2.3 Sample measurements

—2.3.1 Device Preparation

OPV cells with the layered structure ITO/p-type/C60/BCP/Al were fabricated by vacuum deposition. ITO substrates, purchased from Asahi Glass Co., Ltd, with a sheet resistance of 25 Ω/sq were ultrasonicated first in 2-propanol and then in ultra-pure water. They were later exposed to an ultraviolet-ozone surface treatment and transferred to a vacuum chamber. The organic materials were evaporated onto the substrates under a vacuum pressure of less than 10^{-4} Pa, with deposition rates between 1 and 5 $\text{\AA}/\text{s}$. The active area of the diodes was 5.8 mm^2 . The devices were measured in ambient atmosphere with encapsulation.

—2.3.2. J-V measurements

The current density (J) -voltage (V) characteristic was measured for estimation of photovoltaic performance. Current density means that observed current is divided by device area. In order to observe the current flow in organic photovoltaic device, it is applied voltage to organic photovoltaic device which connected voltage source meter (KEITHLEY 2400 series). We swept the voltage from -1 V to +1.5 V at intervals of 0.01 V. When J-V characteristic under light irradiation was measured, we used a spectrum of

AM1.5G [4] (shown in Figure 2.5) and a power density of 100 mW/cm^2 calibrated from standard Si-photodiode. The value of “AM (Air Mass)” means that amount of total air when the sun light passes through. Therefore, sun light spectrum in the atmosphere is AM0 and this value was determined by incident angle to the earth [5] (shown in Figure 2.6). AM1.5G is corresponds to real sunlight-based measurement. To prevent degradation from constituent of the atmosphere, we encapsulated photovoltaic devices in nitrogen globe box before J-V measurement.

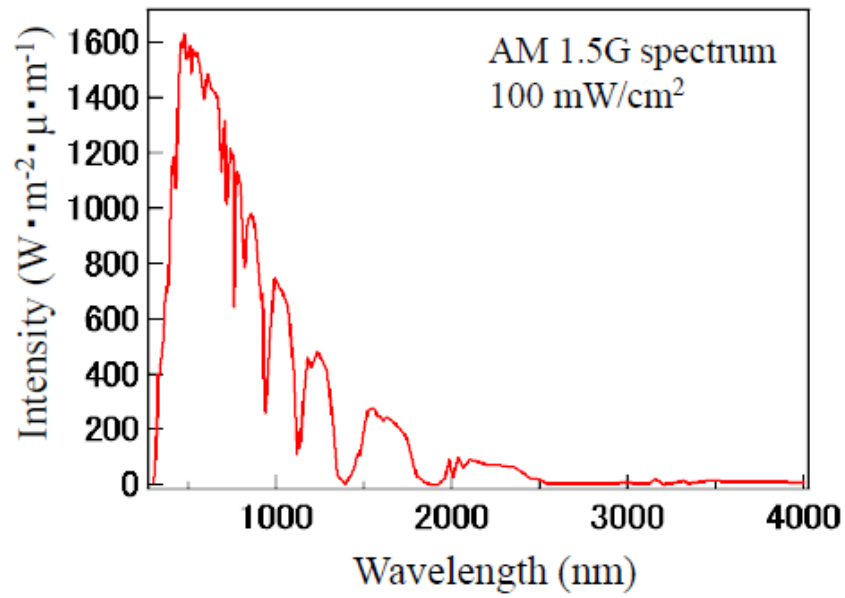


Figure 2.5 AM1.5G spectrum of sun light power 100mW/cm² [5].

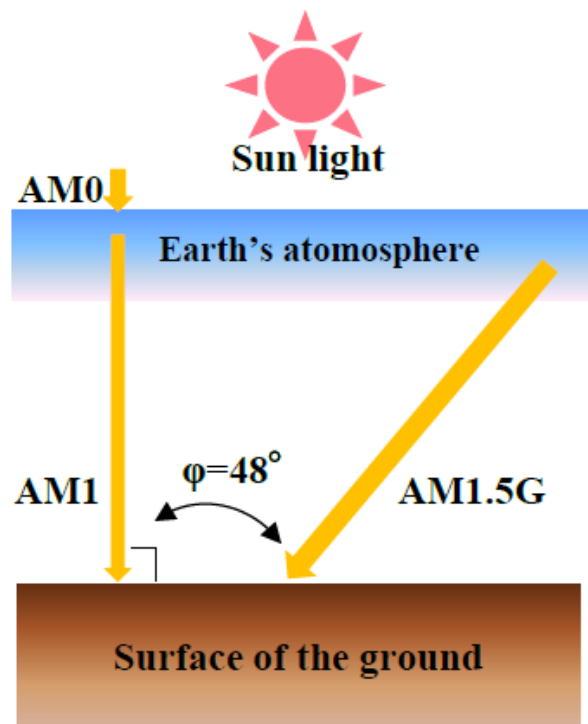


Figure 2.6 Schematic image of “air mass (AM)” definition [6].

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Chapter 3

Carrier Dynamics of p-n Heterojunction Organic Photovoltaic Cells Analyzed by a Novel Graphical Representation of Impedance Spectroscopy

3.1. Introduction

In 1986, Tang fabricated a bilayer heterojunction solar cell with an efficiency approaching 1%, which was a milestone in the development of organic photovoltaic (OPV) cells [1]. Since the innovation of Tang's layered thin film structure, which separates specific functionalities into discrete layers, organic electronic devices have experienced dramatic improvement. In recent years, the power conversion efficiency and the durability of the OPV cells have rapidly improved thanks to the efforts of many researchers [2-5]. However, the carrier dynamics in the OPV cells are still not fully understood because of the complexity of the interactions between each organic layer. By using intensity-modulated photocurrent spectroscopy (IMPS) Forrest *et al.* reported that the donor-acceptor interface interactions in p-n heterostructured OPV cells was governed by the separation of polaron pairs and the carrier recombination rate [6]. Iwamoto *et al.* have analyzed the carrier accumulation behavior using a combination of electric-field-induced second harmonic generation and impedance spectroscopy (IS),

which indicated that the Maxwell Wagner effect is present at the interface between pentacene and C₆₀ [7]. Furthermore, Ishii *et al.* revealed that a giant surface potential (GSP) was present within the organic electron transporting layer deposited on an organic hole transporting layer by means of photoelectron spectroscopy and displacement current measurements [8,9]. To improve device performance, carrier transport analysis of organic heterostructured devices is important. Carrier behavior in organic devices, such as charge separation and recombination, is governed by the interaction of donor–acceptor interfaces because organic materials have very few carriers. Therefore, understanding carrier behavior at the donor–acceptor interface is necessary to further improve organic devices. Standard current-voltage (J-V) measurements only give general information about the carrier transport. To obtain deeper physical insight into the carrier transport, information about the layer-to-layer carrier dynamics in each layer is needed. Impedance spectroscopy is a well-known and fundamental technique to investigate the electric response of structured devices composed of multi-circuit elements [10].

In this study, the basic carrier dynamics in p-n heterostructured OPV cells were investigated using impedance spectroscopy. We introduced a novel representation of the impedance spectrum dynamic modulus plot (DMP), which allowed us to graphically

observe the layer-to-layer carrier injection and carrier accumulation behavior. The diode characteristics of the OPV cells were discussed based on the analysis of the charge carrier behavior by means of DMP analysis in the dark. We revealed the existence of an internal electric field at the donor–acceptor interface, which governs the OPV device performance under the illumination.

3.2. Experimental Methods

—3.2.1. Device Preparation

The compounds TPD, C₆₀ and bathocuproine (BCP) were purchased from Sigma–Aldrich Co. Ltd. Bis-diphenylaminophenyl oligothiophene (BDA-Tn [n=1–3]) derivatives were synthesized using the Suzuki-Miyaura coupling reaction in our laboratory. These materials were purified by vacuum sublimation at 10^{−3} Pa. OPV cells with the layered structure ITO/p-type/C₆₀/BCP/Al were fabricated by vacuum deposition. ITO substrates, purchased from Asahi Glass Co., Ltd, with a sheet resistance of 25 Ω/sq were ultrasonicated first in 2-propanol and then in ultra-pure water. They were later exposed to an ultraviolet-ozone surface treatment and transferred to a vacuum chamber. The organic materials were evaporated onto the substrates under a vacuum pressure of less than 10^{−4} Pa, with deposition rates between 1 and 5 Å/s. The active area of the diodes was 5.8 mm². The devices were measured in ambient atmosphere with encapsulation.

—3.2.2. Device Characterization

The highest occupied molecular orbital (HOMO) energy levels of the organic materials were determined by photoelectron yield spectroscopy in air using an AC-3 spectrometer (Riken Keiki Co. Ltd., Japan). The film absorption spectra were recorded by a UV-3600 UV-Vis-NIR spectrophotometer (Shimadzu Co. Ltd., Japan). The optical band gaps were estimated from the absorption edge of the thin films. The lowest unoccupied molecular orbital (LUMO) energy levels were estimated by the subtraction of the optical band gap from the HOMO levels.

The J-V characteristics of the devices were measured at room temperature with a source measurement unit (Keithley Instruments Inc., 2400) in the dark and under illumination of 100 mW/cm² white light provided by a 1.5 AM solar simulator.

The impedance measurements were performed with an impedance analyzer (Agilent Technologies Inc., 4294A) in the frequency range from 100 Hz to 1 MHz in the dark.

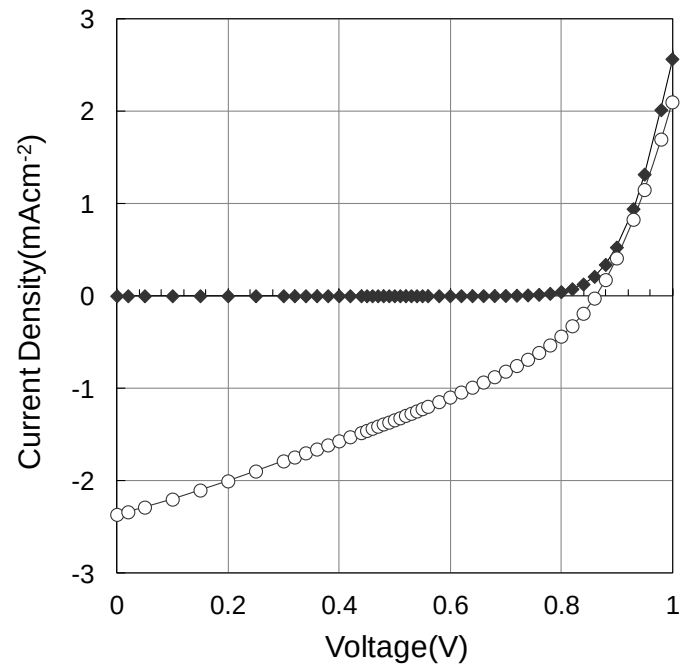
The AC modulation amplitude was kept as low as 50 mV, where the response to the AC amplitude was linear. The complex impedance data were transferred to a PC and processed mathematically to appropriate representations.

3.3. Results and Discussion

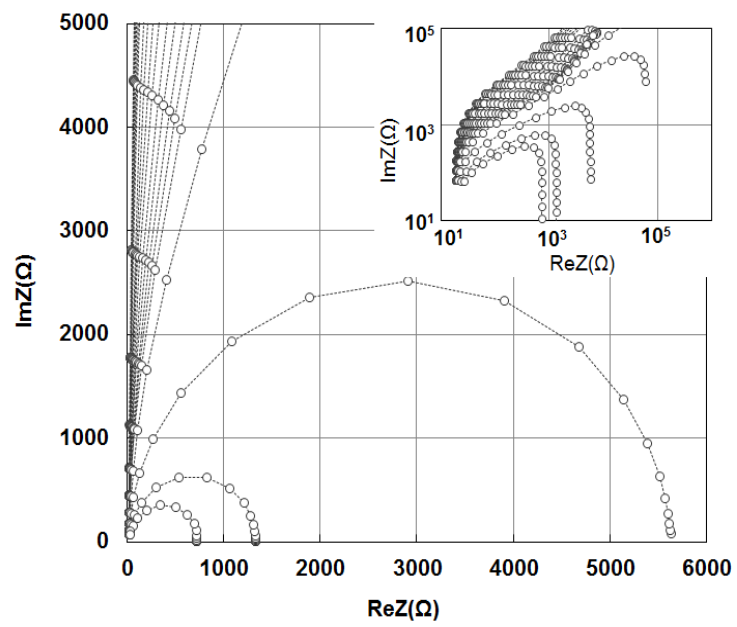
—3.3.1. Equivalent Circuit Model and Modulus Plot of p-n Heterostructured OPV Cell

Figure 3.1(a) shows the J-V characteristics of the p-n heterostructured OPV cell. The OPV cell had an open-circuit voltage (V_{oc}) of 0.86V, a short-circuit current density (J_{sc}) of 2.37 mAcm^{-2} , a fill factor (FF) of 33%, and a power conversion efficiency (η) of 0.67% under AM1.5, 100 mWcm^{-2} simulated solar light. Impedance and modulus Cole–Cole plots of the OPV cell are shown in Figure 3.1(b) and 3.1(c). The advantage of using modulus over impedance is that it is a unified view of the Cole–Cole plot, which makes clear the equivalent circuits, and the Mott–Schottky plot, which indicates the accumulation behavior of the carriers. As shown in Figure 3.1(c), some semicircles were observed in the modulus Cole–Cole plot. In this case, the change of the semicircle radius represents how deep the carrier accumulates in the layer. The impedance Cole–Cole plot provided the resistance information about the OPV devices for several layers. While only one arc was observed in the impedance Cole–Cole plot, several arcs corresponding to the different layers were clearly identified in the modulus Cole–Cole plot (Figure 3.1[c]).

(a)



(b)



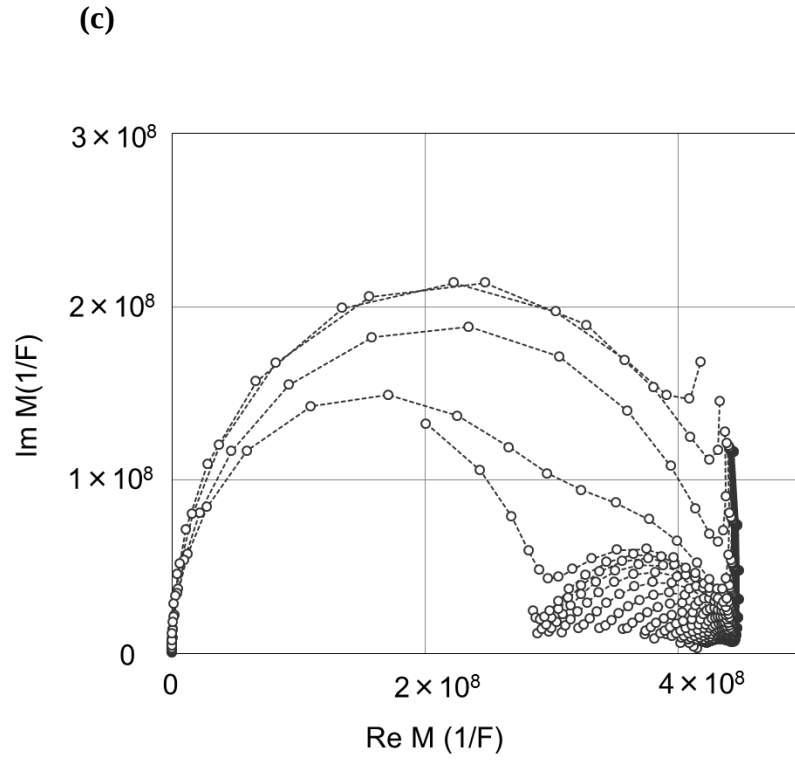


Figure 3.1 Current density-voltage characteristics and the applied voltage dependence of Cole–Cole plot of the OPV cell, ITO/mTPD/C60/BCP/Al. (a) J–V characteristic. (b) Impedance Cole–Cole plot (the inset shows the logarithmic display). (c) Modulus Cole–Cole plot.

In Figure 3.2, the modulus data of the OPV cell in the dark condition under 0.7 V bias were fitted by the simple equivalent circuit models. The equivalent circuit of p-n heterostructured OPV cells was explained by the model which is connected with CR parallel circuits of three layers corresponding to an individual layer.

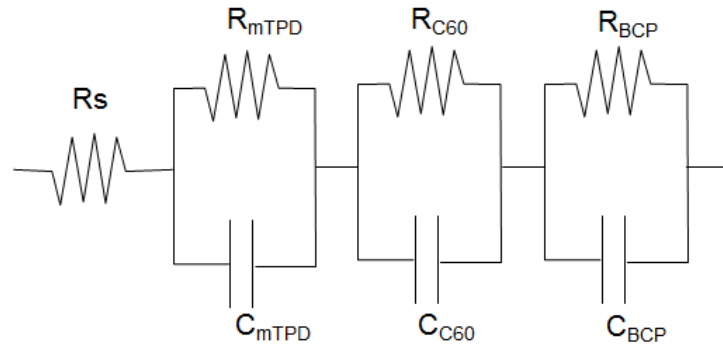
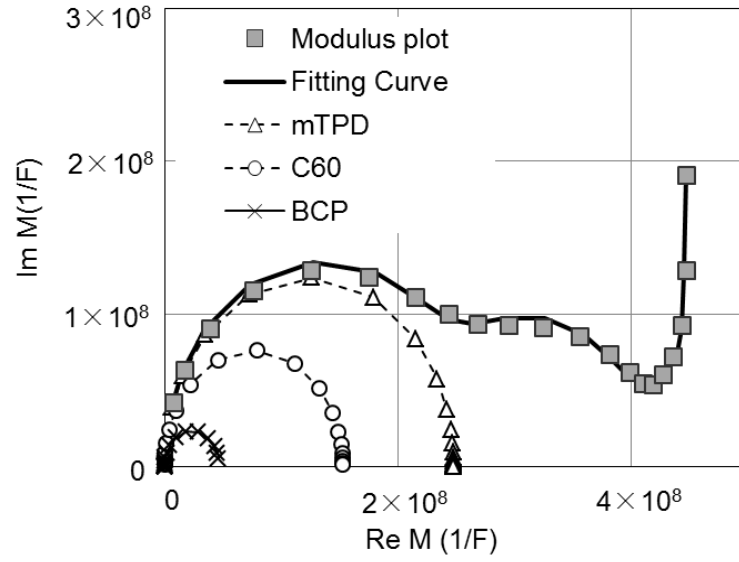


Figure 3.2 Experimental modulus plot and best fitting curve by the equivalent circuit model under 0.7 V bias.

—3.3.2. DMP of p-n Heterostructured OPV Cells

Figure 3.3 shows examples of the DMP of the OPV p-n cells with different layer thicknesses. The structure of the devices was ITO/mTPD(X)/C₆₀(60-X)/BCP/Al, in which layer thickness X was changed from 20, 30 and 40 nm respectively. As shown in this figure, the inverse of capacitance at high frequency (right-hand edge) is mostly constant, which corresponds to the invariance of the device against applied voltage over the range of layer thicknesses measured. From this figure, it is easy to determine at which voltage and to which layer the carriers accumulate.

From DMP, changes to the circuits of OPV devices can be seen. At sufficiently low bias voltage, there is only a small semicircle and a vertical line at the high frequency side. The vertical line means the device is an insulator and the electric response is purely dielectric. As the bias voltage increases, several semicircles appear and merge. The small semicircles correspond to p-type and n-type organic layers in which carriers were injected and were conductive. The equivalent circuits of the devices changed to a parallel connection of resistance and capacitance from pure capacitance. Finally, only one semicircle remained at sufficiently high voltage. There was a small semicircle at the high frequency side below a bias voltage of -1.0 V in all three devices. Compared with the designed thickness, the semicircle was assigned to a BCP layer. It is surprising that

electrons accumulate in the BCP layer at such low bias voltages. The carrier accumulation in a BCP layer adjacent to a C_{60} layer was confirmed by photoelectron yield spectroscopy and displacement current measurements [9]. The semicircle that appeared at the high frequency side was assigned to the C_{60} layer and the semicircle that appeared at the lower frequency side was assigned to the mTPD layer. The assignment is obvious because the radius at the lower frequency side is proportional to the designed mTPD thickness. In Figure 3.3, as the mTPD layer thickness increases, the radius of the semicircle at the lower frequency increases.

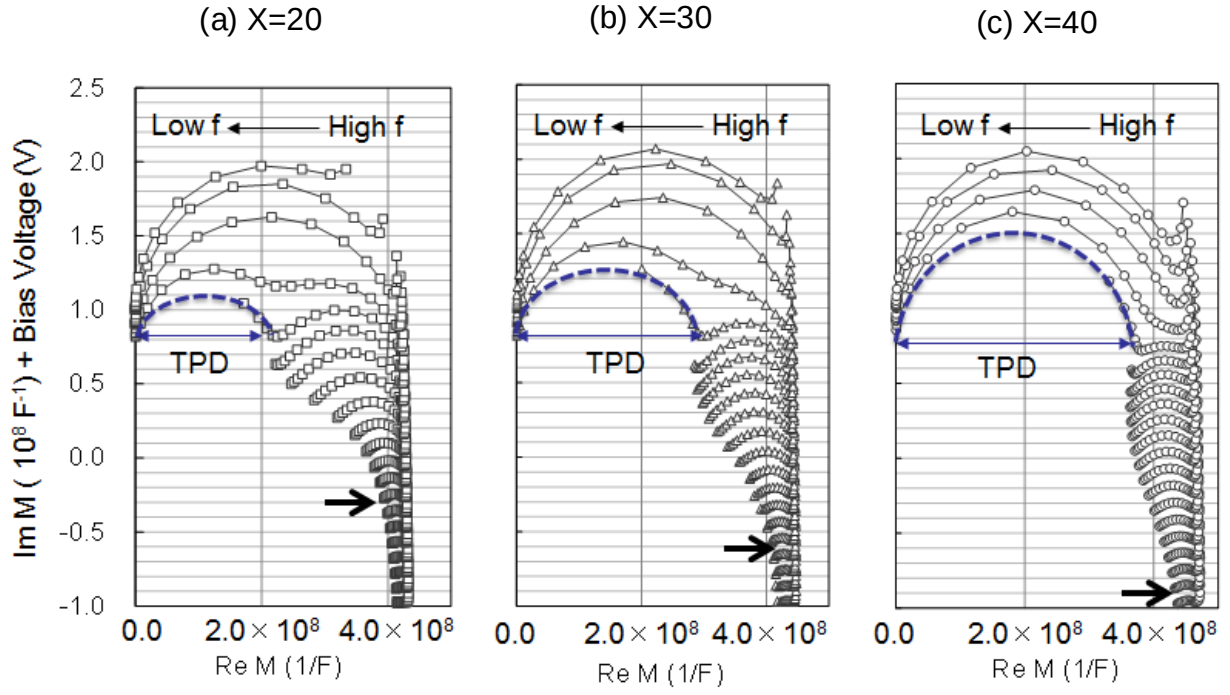


Figure 3.3 Dynamic modulus plot (DMP) (Cole–Cole) of the OPV cells, ITO/mTPD(X)/C₆₀(60-X)/BCP/Al, (a) X=20, (b) X=30 and (c) X=40. Dot semicircles correspond to the TPD layer thickness. Arrows show the threshold voltage at which carrier accumulation in the C₆₀ layer starts.

The radius of the semicircle at higher frequency becomes smaller by decreasing the layer thickness of the C_{60} layer. The separation of these two semicircles comes from the Maxwell–Wagner effect, i.e. the difference in the relaxation time in each layer [7]. After injection, the two semicircles merge to one semicircle. Because the voltage is applied mainly to the highest resistance layer, the conductivity increase is greater than that of lower resistance layer. Because the conductivity and the relaxation time balance at high voltage, all the semicircles coalesce into one. The change of the electric properties of each layer in multilayered devices can be understood graphically from the DMP. In Figure 3.3(b), the semicircle becomes larger as the bias voltage increases from -1.0 to 0.7 V, which means the thickness of the conductive C_{60} layer becomes larger through carrier accumulation. As the voltage increases, a small semicircle evolves and increases its radius. After its radius saturates, a new semicircle evolves from 0.7 V (the voltage is mostly independent of the layer thickness). This is the start of carrier injection into the mTPD layer. These two semicircles merged to one semicircle at high voltage. This value corresponds to the threshold voltage of current density increase in J-V characteristics of this device. The accumulation of electrons in C_{60} starts at -0.3 V ($x=20$ nm), -0.6 V ($x=30$ nm), and -0.9 V ($x=40$ nm), as indicated by lines in Figure 3.3. The threshold voltage (V_{th}) at which accumulation in the C_{60} layer starts is proportional to the layer

thickness. It means that a constant internal electric field exists in the OPV cells. When we differentiate the voltage shift against the layer thickness, the internal electric field was estimated to be 30 mV/nm. The corresponding surface charge density is 0.80 mC/m² using a dielectric constant of 3.0. This carrier accumulation behavior at the organic hetero-interfaces has been observed in multilayer organic light-emitting diodes (OLEDs) [11,12]. Interface charge was first detected by Brütting *et al.* at the a-NPD/Alq3 interface in a bilayer OLED. Furthermore, Ishii *et al.* reported clear GSP behavior with a slope of 48 mV/nm, which corresponds to an interface charge density of 1.36 mC/m² [13]. In our study, the carrier accumulation at the TPD/C₆₀ interface was observed by the DMP analysis, which is similar to previous reports. With DMP analysis we can observe complex charge accumulation behavior at a glance without any simulation. Because this internal electric field can suppress the charge dispersion along the donor–acceptor interface in the dark condition of the OPV cells, the reduction of the internal electric field is quite important to improve of the diode characteristics of OPV cells.

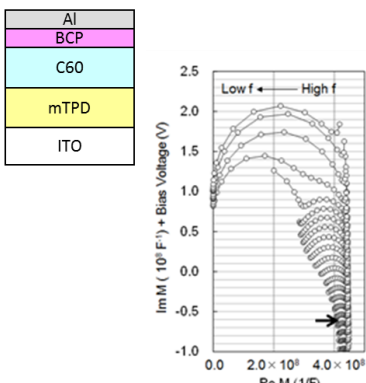
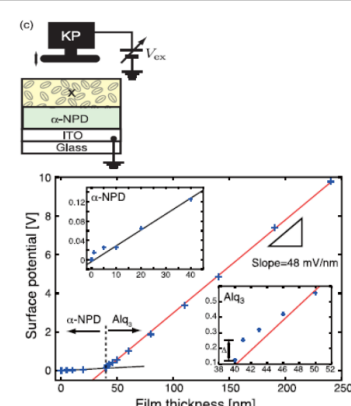
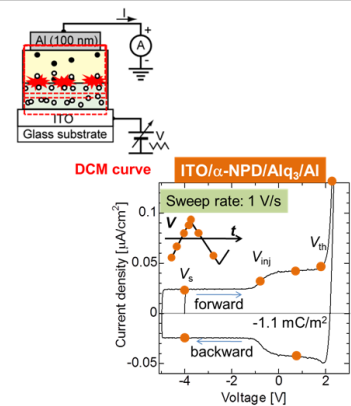
Advanced IS analysis Dynamic modulus plots (In this study)	Kelvin probe method J. Appl. Phys. 111, 114508 (2012)	Displacement Current method Appl. Phys. Lett. 92, 203306 (2008)
		
Internal electric field 30 (mV/nm)	Internal electric field 48 (mV/nm)	Internal electric field 34 (mV/nm)
Interface charge density 0.80 (mC/m ²)	Interface charge density 1.4 (mC/m ²)	Interface charge density 1.1 (mC/m ²)

Figure 3.4 Comparison of the methods for calculation of the internal electric field and interface charge density.

—3.3.3. DMP with Varied p-type Materials

The charge accumulation properties of bilayer devices composed of new p-type materials, bis-diphenylaminophenyl oligothiophenes (BDA-Tn), were examined by impedance spectroscopy. Oligothiophenes are one of the largest families of organic semiconductors, and have been widely used in OPVs because of their high charge-carrier mobility and facile synthesis for tuning energy levels [14]. We have investigated the dependence of PCE on the conjugation length by the incident photon-to-electron conversion efficiency (IPCE) action spectrum.

The new donor materials BDA-Tn were expected to show high PCEs, because their conjugation lengths are longer than mTPD, i.e. they can absorb more of the AM1.5 spectrum. To investigate the effect of conjugation length, we inserted different numbers of thiophene units into the TPD skeleton.

Figure 3.5 shows the typical current density-voltage characteristics of the OPV cells based on the BDA-Tn derivatives, BDA-T0($\circ$), BDA-T1($\bullet$), BDA-T2($\blacktriangle$), BDA-T3($\blacklozenge$) under illumination of AM 1.5, 100 mWcm^{-2} . The structures of the devices were ITO/BDA-Tn/ C_{60} /BCP/Al. The photovoltaic parameters are listed in Table 3.1.

As the number of thiophene units increases, V_{oc} of the BDA-Tn/ C_{60} cells was reduced and the J_{sc} and FF improved significantly. The highest power conversion efficiency in

this series of materials was achieved with BDA-T3, which reached 1.33%.

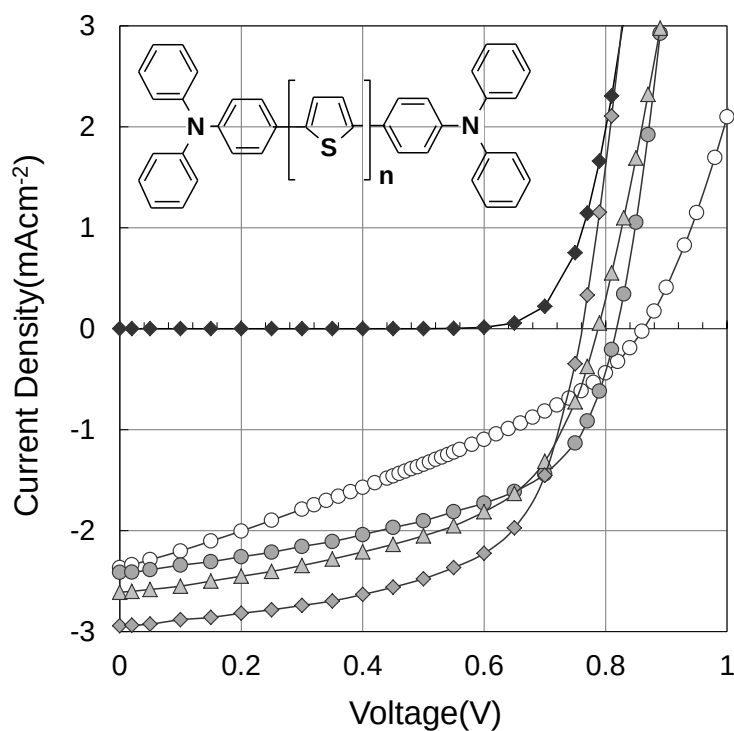


Figure 3.5 Current density-voltage characteristics of the OPV cells based on the BDA-Tn derivatives, BDA-T0($\circ$), BDA-T1($\bullet$), BDA-T2($\blacktriangle$), BDA-T3($\blacklozenge$) under illumination of AM1.5, 100mWcm^{-2} . The inset shows the chemical structures of the BDA-Tn derivatives.

Table 3.1 Photovoltaic performance of ITO/BDA-Tn/C60/BCP/Al under illumination of AM1.5, 100 mWcm⁻².

	Voc	Jsc	FF	η	Ip	Af
	(V)	(mA cm ⁻²)		(%)	(eV)	(eV)
BDA-T0	0.86	2.37	0.33	0.67	5.5	2.5
BDA-T1	0.82	2.42	0.53	1.05	5.4	2.7
BDA-T2	0.79	2.62	0.53	1.09	5.4	3.0
BDA-T3	0.76	2.94	0.59	1.33	5.3	3.1

The reduction of the Voc was attributed to the relatively low ionization potential of the BDA-Tn materials. The improvement of the Jsc was caused by the stronger absorption of the solar light. BDA-T3, which has three thiophene units, exhibited an absorption peak around 440 nm which is a bathochromic shift of ~30 nm compared with mTPD ($\lambda_{\text{max}} = 410$ nm).

The layer resistivity is closely related to the carrier mobility of the material and the FF in OPV cells. We measured the mobilities of the BDA-Tn derivatives by TOF methods. The measured mobilities of the BDA-Tn derivatives were $1.0 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (BDA-T0 or mTDP), $4.8 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (BDA-T1), $1.6 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (BDA-T2), and $4.9 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (BDA-T3). It is puzzling that the mobilities decrease as the number of thiophene units increases, whereas the FF improves with the number of thiophene units. Generally, TOF measurements are carried out with a high electric field, but OPV cells are driven under very low electric fields (so called built-in potentials). These electric field differences may make it difficult to interpret the TOF results.

To understand why the FF improves, we have carried out an impedance analysis of the OPV cells composed of BDA-Tn derivatives. In Figure 3.5, the accumulation of electrons in C₆₀ starts at -0.6 V (BDA-T0), -0.4 V (BDA-T1), -0.3 V (BDA-T2), and -0.1 V (BDA-T3), as indicated by lines. As the number of thiophene units increases, the

V_{th} of carrier accumulation in the C_{60} layer becomes higher (Figure 3.6). The change of these threshold voltages V_{th} means the change of the internal electric field in each OPV cell. The more thiophene units there are, the smaller the internal electric field in the OPV cell becomes. The internal electric field works to disturb the carrier transport to the each electrode. We speculate that reduction of the internal electric field is the reason for the improvement of the FF in OPV cells.

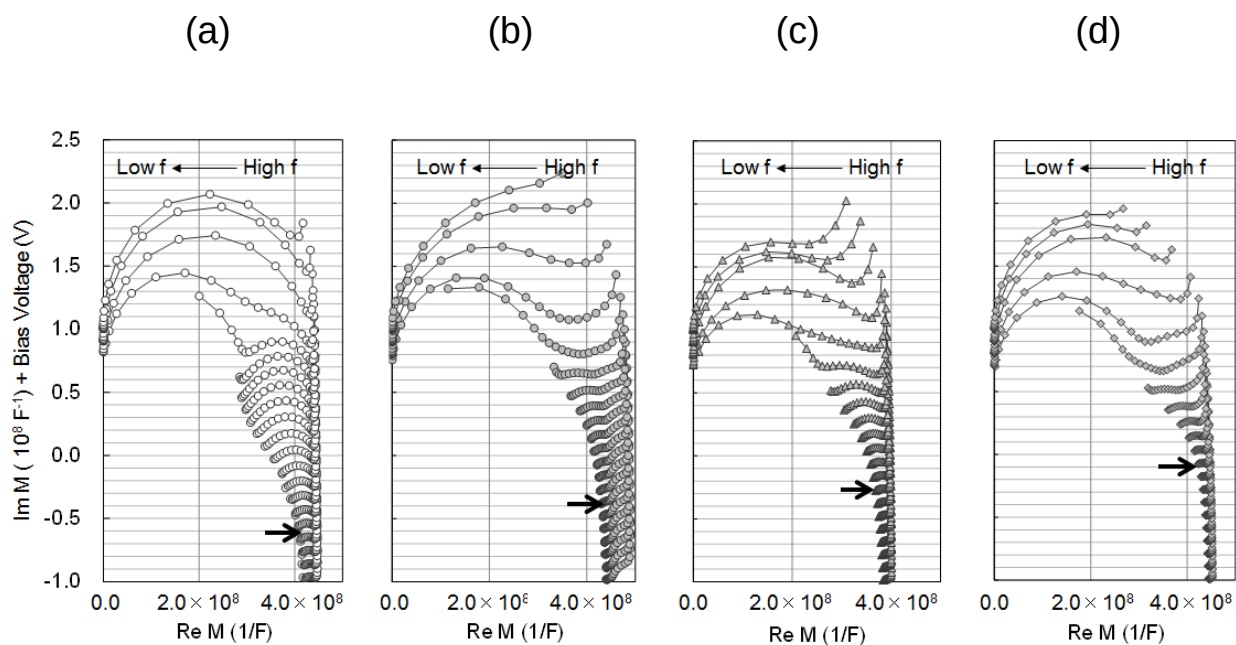


Figure 3.6 Dynamic modulus plot (DMP) (Cole-Cole) of the OPV cells based on the BDA-Tn derivatives, BDA-T0 ($\circ$), BDA-T1 ($\bullet$), BDA-T2 ($\blacktriangle$), BDA-T3 ($\blacklozenge$). Arrows show the threshold voltage at which carrier accumulation in the C60 layer starts.

3.4. Summary

In this work, we have investigated the impedance response of TPD/C₆₀ p-n hetero-structured OPV cells against applied voltages. The equivalent circuit of p-n hetero-structured OPV cells can be explained by three connected CR parallel circuits, each of which corresponds to a layer of the device.

As a result of the modulus analysis, the threshold voltage for charge injection and accumulation within the C₆₀ layer varied in proportion to the film thickness. We have found that a constant internal electric field exists which disturbs the carrier transport to the electrodes in OPV cells because of interactions at the donor–acceptor interface. It is thought that this internal electric field is the reason for the reduction of the FF of OPV cells.

Next, new donor materials BDA-Tn were investigated. By increasing the number of thiophene units in BDA-Tn the power conversion efficiency and FF increased significantly, from 33% to 59%. Based on the DMP analysis, we found that the internal electric field decreased by introducing more thiophene units and concluded that the reduction of the internal electric field was the reason for the improved device performance. Further investigation of this phenomenon to reduce the internal electric field will potentially lead to higher-efficiency organic heterostructured solar cells.

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Chapter 4

In-situ Measurements of the Photoconductivity of Multi-layered Organic Photovoltaic Cells

4.1. Introduction

Impedance spectroscopy (IS) is a powerful tool for analyzing the electrical properties of devices, in particular for capacitance-voltage analyses, which have become standard methods to investigate device characteristics. Recently, IS has also been extensively applied to organic devices, such as organic light-emitting diodes [1-5], organic photovoltaic (OPV) cells [6,7] and organic thin-film transistors [8,9], revealing the electrical properties including the carrier injection [1,2] and charge transport properties [3-5].

Along with IS measurements, other methods have been used to measure the mobility in highly resistive organic semiconductor films and other materials including the time-of-flight (TOF) method [10,11], the dark injection (DI) transient method [12-15], a method to obtain the mobility from the I-V characteristics of the space charge limited current (SCLC), time-resolved electroluminescence (EL) spectroscopy [16], and the photo-excited time-resolved microwave conductivity technique [17,18].

To accurately evaluate the transit time using the TOF and DI methods, a film that is

substantially thicker than the light-emitting layer in an organic EL device is required. Because the electronic and optical properties of an organic semiconductor largely depend on the film thickness [19], measurements should be performed on a film thickness equal to that in an actual device. In the SCLC method, measurements using the actual device structure are difficult and the electric-field dependence of the mobility cannot be determined. Time-resolved EL spectroscopy and photo-excited time-resolved microwave conductivity are methods used to evaluate the mobility under conditions that differ from the actual applied voltage.

In contrast, IS measurements that enable the mobility to be measured in actual OPV devices and the electric-field dependency of the mobility can be evaluated. However, the photoconductivity in the low-voltage region, where an actual OPV device operates, has not been discussed. In all cases, the evaluation of the mobility under high-electric-field conditions, such as in the SCLC region, has been the main focus of discussion.

In this study, in situ IS measurements of the photoconductivity of the carriers induced by photo-irradiation in the layers in organic heterojunction-structured photovoltaic devices were performed. The IS measurements were carried out by changing the externally applied voltage and the intensity of the light irradiating the device. To

establish a basic method, using the dependence of the frequency characteristics of the relaxation time on the light intensity, a change in the photo conductivity that originated from the carriers induced by photo-irradiation in each layer was examined using a donor/acceptor hetero-structured device.

4.2. Experimental Methods

—4.2.1 Device Preparation

The compounds CuPc, C₆₀ and bathocuproine (BCP) were purchased from Sigma–Aldrich Co. Ltd. These materials were purified by vacuum sublimation at 10⁻³ Pa. OPV devices with a layered structure were fabricated by vacuum deposition. The device structure was: indium tin oxide (ITO)/30-nm copper phthalocyanine (CuPc)/60-nm C₆₀/10-nm bathocuproine (BCP)/100-nm Al. ITO substrates, purchased from Asahi Glass Co., Ltd, with a sheet resistance of 25 Ω/sq were ultrasonicated first in 2-propanol and then in ultra-pure water. They were later exposed to an ultraviolet-ozone surface treatment and transferred to a vacuum chamber. The organic materials were evaporated onto the substrates under a vacuum pressure of less than 10⁻⁴ Pa, with deposition rates between 1 and 5 Å/s. The active area of the diodes was 5.8 mm². The devices were measured in ambient atmosphere with encapsulation.

—4.2.2 Device Characterization

The J-V characteristics of the devices were measured at room temperature with a source measurement unit (Keithley Instruments Inc., 2400) in the dark and under illumination of 100mW/cm^2 white light provided by a AM 1.5 solar simulator.

The impedance measurements were performed with an impedance analyzer (Agilent Technologies Inc., 4294A) in the frequency range from 100 Hz to 1 MHz in the dark. The AC modulation amplitude was kept as low as 50 mV, where the response to the AC amplitude was linear. The complex impedance data were transferred to a PC and processed mathematically to appropriate representations.

4.3. Results and Discussion

Figure 4.1(a) shows the configuration of the donor/acceptor heterostructured OPV device used in this study, the generation of an exciton accompanied by photoirradiation, and the process of generating holes and electrons at the interface between the donor and acceptor layers. Figure 4.1(b) shows the dependency of the J-V characteristics on the light intensity. Under 1 sun of irradiance, the device characteristics were: open circuit voltage, $V_{oc} = 0.48$ V, space charge current density, $J_{sc} = 3.4 \text{ mAcm}^{-2}$, fill factor, $FF = 0.46$, and the power conversion efficiency, $PCE = 0.75\%$.

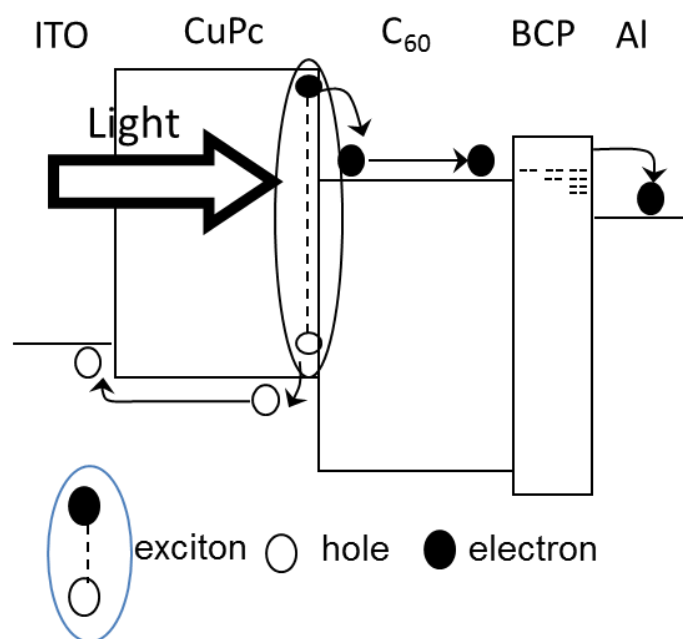


Figure 4.1(a) Schematic energy diagram of the CuPc/C₆₀ p-n hetero-junction photovoltaic device. (The structure of the device: ITO/30 nm CuPc/60 nm C₆₀/10 nm BCP/100 nm Al.)

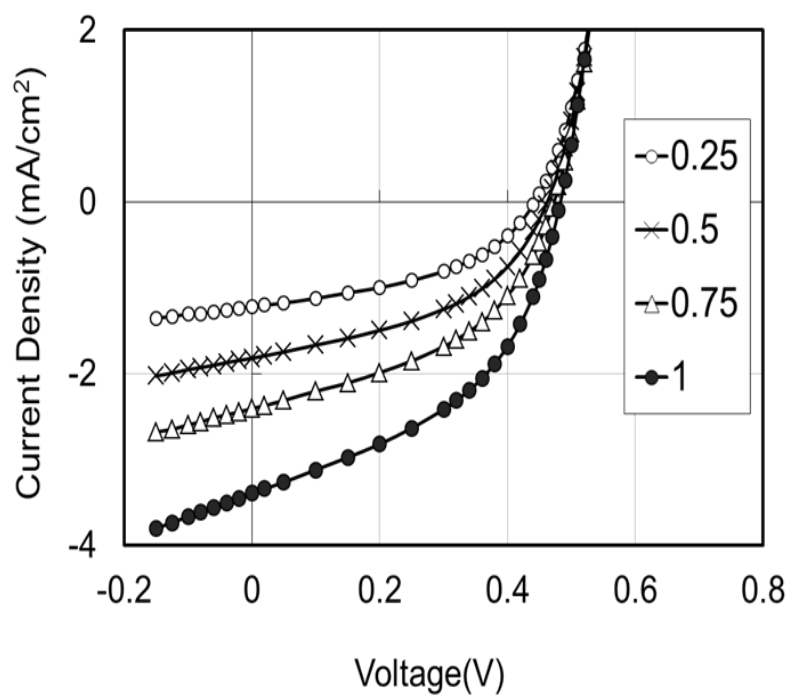


Figure 4.1(b) J-V characteristics of an organic solar cell in the dark and under various illumination intensities of an AM1.5G simulated solar spectrum.

The threshold voltage was determined to be about 0.5 V from the J-V characteristics (this is the voltage at which a large number of charges begin to be injected from the electrodes). The voltage range in which the device generates power as an OPV device, that is, the region where it operates, was 0–0.5 V. This voltage range was smaller than the bias voltage at which the mobility and conductivities are evaluated at using conventional methods. This demonstrates the importance and necessity to evaluate the conductivity and carrier mobility within the actual driving-voltage region of an OPV, which is the purpose of this study.

Figure 4.2 shows Bode modulus plots for each bias voltage under 1 sun of irradiance, that is, the characteristics of the imaginary part of the modulus ($\text{Im } M$) versus frequency. A change in the resistance component was observed because $M \sim i\omega Z$, where ω is the angular frequency and i is the imaginary part.

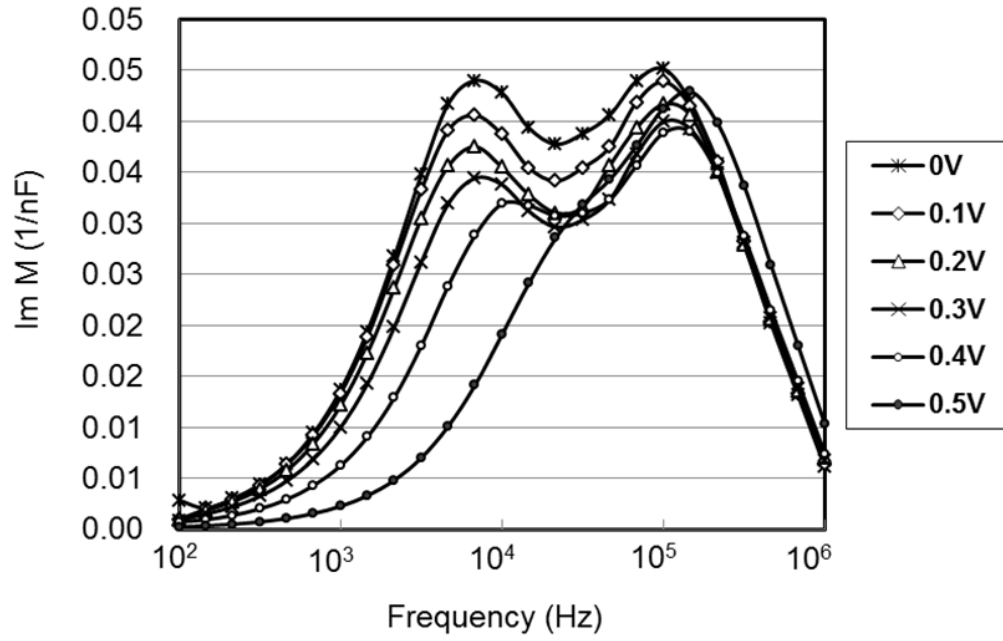


Figure 4.2 Bode modulus plots for each bias voltage under 1 sun of irradiance, that is, the characteristics of the imaginary part of the modulus ($\text{Im } M$) versus frequency.

There are two components, each with a relaxation time that responds to the frequency.

The time constants for these two components did not change in the region from 0 to 0.4 V, which is equal to or below the threshold voltage. The conductivity within this voltage region depended on the frequency response.

From the formulas:

$$\tau = \frac{1}{2\pi f_{peak}} = RC \quad (4.1)$$

where τ is the relaxation time, and $C = \epsilon S/d$

$$\sigma = \frac{1}{\rho} = \frac{d}{RS} \quad (4.2)$$

where S is the area and d is the thickness of the layer

The peak frequency was derived from the following equation:

$$f_{peak} = \frac{2\pi}{\epsilon} \sigma \quad (4.3)$$

where σ is the conductivity, ρ is the electrical resistivity, ϵ is the permittivity.

In the Bode plots, there was a proportional relationship between f_{peak} and σ .

Figure 4.3(a) shows the dependency of the Bode plots on the light intensity at a bias voltage of 0.3 V. The peak frequencies of the two components shifted, which is in agreement with the changes in the photo-induced carriers that were generated according to the light intensity. Figure 4.3(b) shows plots of the peak frequency versus light intensity.

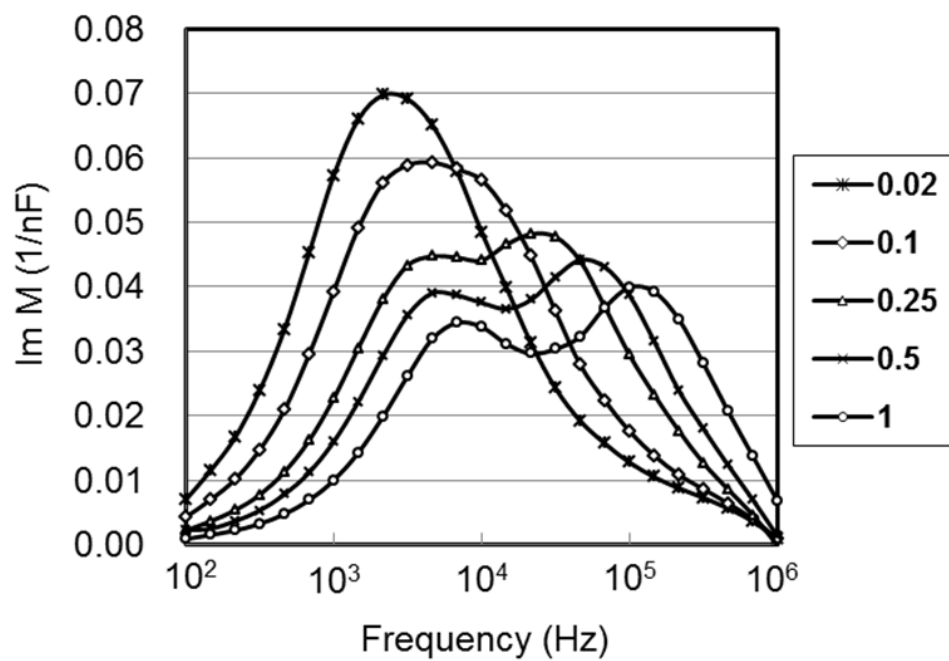


Figure 4.3 (a) Dependence of the Bode plots on the light intensity at a bias voltage of 0.3 V.

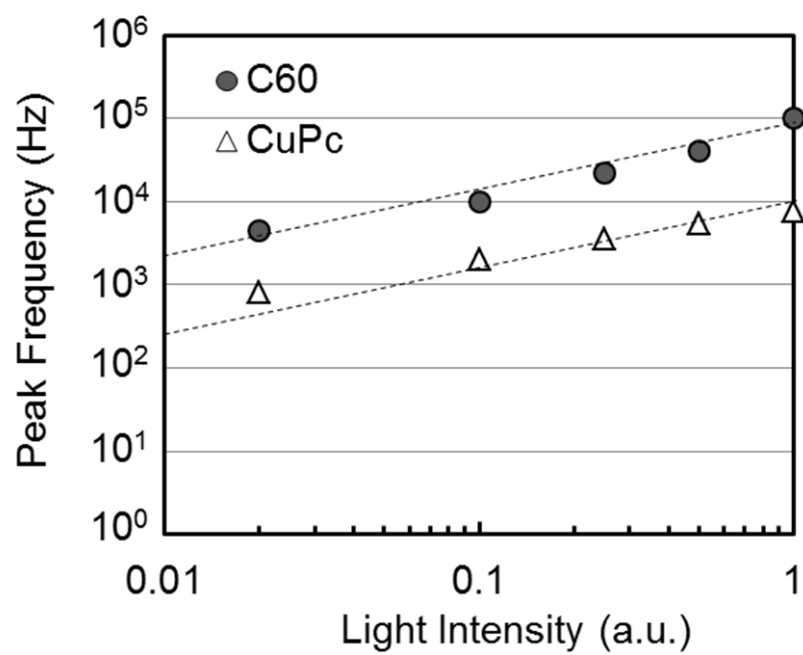


Figure 4.3 (b) Dependence of the peak frequency on the light intensity.

The changes in the slopes for the two components were the same, which indicates that the main change was a shift in the conductivity of each layer, caused by holes and electrons being generated in equal amounts under light irradiation (Figure 4.1 (a)). The components of the relaxation time were identified from the dependency of the film thickness for each layer. The component in the low-frequency region was found to be CuPc and that in the high-frequency side was found to be C₆₀. Given that the ratio of the peak frequency was a single digit, the ratio between the carrier mobility of the CuPc layer and the C₆₀ layer was calculated to be a single digit using the formula:

$$\sigma = \mu \cdot n \cdot e \quad (4.4)$$

where μ is the carrier mobility, n is the carrier density and e is the elementary charge.

Figure 4.4 shows the σ_{AC} values (AC electrical conductivity) at bias voltages from 0 to 0.5 V for an OPV device under 1 sun of irradiance.

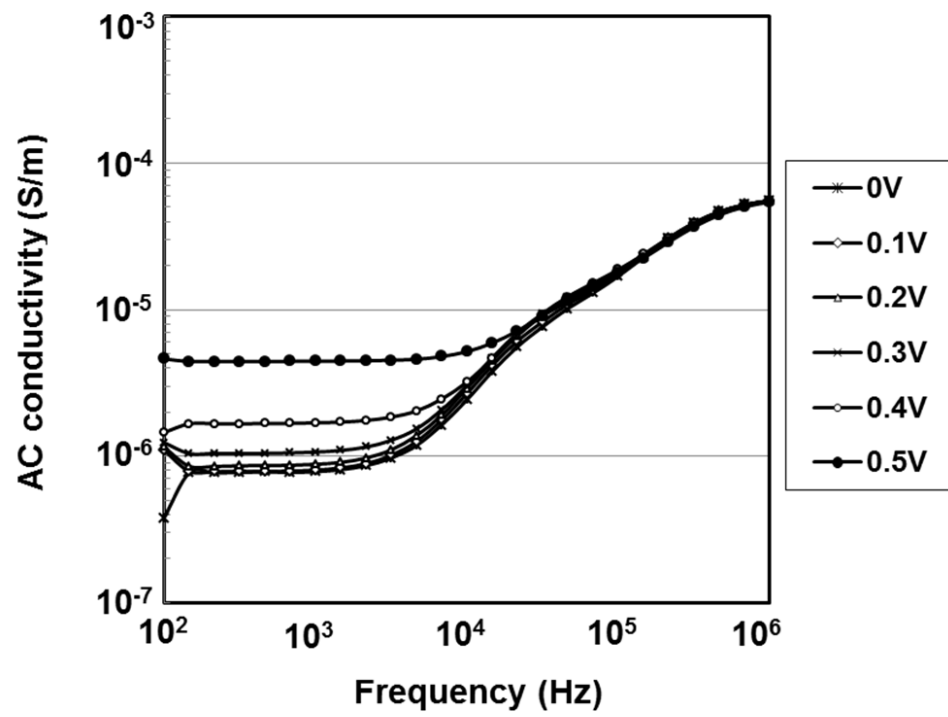


Figure 4.4 Frequency dependence of the AC conductivity under different DC bias voltages.

Using $\sigma_{AC} = d/A \cdot Z$, the conductivity of the entire device was determined to be 1.0 $\mu\text{S/m}$ at 100 Hz. The μ of the device was calculated to be on the order of $10^{-3} \text{ cm}^2/\text{Vs}$ using $n = 10^{16} \text{ m}^{-3}$. This has also been used in other studies to evaluate the conductivities of other Pc systems. Therefore, because the mobility ratio between CuPc and C_{60} was only a single digit, the mobility of CuPc was calculated to be in the order of $10^{-4} \text{ cm}^2/\text{Vs}$, and that of C_{60} was in the order of $10^{-3} \text{ cm}^2/\text{Vs}$. These values agree well with the previously reported results evaluating the mobility of each material.

4.4. Summary

In-situ impedance spectroscopy (IS) observations of the photoconductivity of the carriers induced by photoirradiation in organic heterojunction-structured photovoltaic devices are presented. Analyzing the IS data showed the existence of two components with different relaxation times, which originated from the donor and acceptor materials. The peak frequency of these components shifted as a function of the light intensity and they had the same slope. The conductivity originated from the holes and electrons that were photo-induced by photoirradiation and was used to calculate the mobility ratio. The mobilities of the CuPc and C₆₀ layers were calculated from the conductivities and were in the orders of 10^{-4} and 10^{-3} cm²/Vs, respectively. For the first time, in situ measurements of the photoconductivity were performed using an actual device in the low-voltage region in which OPV devices are operated. These results serve as a guideline for the future development and improvement of organic semiconductor devices based on multilayer structures.

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Chapter 5

General Conclusion

Organic photovoltaic cells (OPVs) as a renewable energy source have attracted much attention due to their ease of manufacture, low cost, flexibility and so on. In 1986, Tang fabricated a bilayer heterojunction solar cell with an efficiency approaching 1%, which was a milestone in the development of organic photovoltaic (OPV) cells. Since the innovation of Tang's layered thin film structure, which separates specific functionalities to discrete layers, OPV cells have experienced dramatic improvement. In recent years, the power conversion efficiency and the durability of the OPV cells have rapidly improved thanks to the efforts of many researchers. However, the carrier dynamics in the OPV cells are still not fully understood because of the complexity of the interactions between each organic layer. To improve device performance, carrier transport analysis of organic hetero-structured devices is quite important. Carrier behavior in OPV cells, such as charge separation and recombination, is governed by the interaction of donor–acceptor interfaces because organic materials have very few carriers. Therefore, understanding carrier behavior at the donor–acceptor interface is necessary to further improve OPV cells.

Standard current-voltage (J-V) measurements only give general information carrier

transport. To obtain deeper physical insight about carrier transport, information about the layer-to-layer carrier dynamics in each layer is needed. Impedance spectroscopy (IS) is a well-known and fundamental technique to investigate the electric response of structured devices composed of multi circuit elements.

In this study, the basic carrier dynamics in p-n hetero-structured OPV cells were investigated by impedance spectroscopy. We introduced a novel representation of impedance spectrum dynamic modulus plot (DMP), which allowed us to graphically observe the layer-to-layer carrier injection and carrier accumulation behavior.

In Chapter 3, the diode characteristics of the OPV cells were discussed based on analyzing the charge carrier behavior by means of DMP analysis in the dark condition.

We revealed the existence of an internal electric field which disturbs the carrier transport to the electrodes at the donor–acceptor interface, which governs the OPV cell performance under the illumination. It is thought that this internal electric field is the reason for the reduction of the FF of OPV cells.

In Chapter 4, under the light irradiation, we have succeeded in-situ measurement of photo-conductivity of each layer in the p-n hetero-structured OPV cells by using IS methods. The carriers were generated at the donor-acceptor interface by the dissociation process of excitons. Therefore, the same amount of holes and electrons were generated

into each layer of OPV cells. Photo conductivity dependence within each layer on light intensity was investigated. The mobility ratio can be evaluated from the ratio of the conductivity shifts each of which corresponds to a layer of the cell. The mobility ratio corresponds well the already reported values.

Further investigation of this phenomenon to reduce the internal electric field will potentially lead to higher-efficiency organic hetero-structured solar cells. Moreover, IS methods are a useful technique to elucidate the layer-to-layer carrier dynamics in OPV cells. We hope that develop new technology and new products based on achievements in this thesis. Then, we will be happy if the achievements provide further development of organic photovoltaic technology and science.

— List of Publications and Presentations —

[Papers]

- [1] Ryoji Maeda, Hiroshi Tokairin, Hidetsugu Ikeda, Jun-ichi Takahashi and Yuji Yoshida “Carrier dynamics of p-n heterojunction organic photovoltaic cells analyzed by a novel graphical representation of impedance spectroscopy” *Advances in Materials Physics and Chemistry (AMPC)* 2015, 5, 1-9, DOI: 10.4236/ampc.2015.51001
- [2] Ryoji Maeda, Hiroshi Tokairin, Jun-ichi Takahashi and Yuji Yoshida “In-Situ Measurements of the Photoconductivity of Multi-Layered Organic Photovoltaic Devices Using Impedance Spectroscopy” *Advances in Materials Physics and Chemistry (AMPC)* 2015, 5, 47-52, DOI: 10.4236/ampc.2015.52007

[Presentations: Domestic Conference]

- [1] Ryoji Maeda, Shintaro Iwamoto, Masahide Matsuura, Hiroaki Nakamura, Hidetsugu Ikeda, “Using as p-type of organic semiconductors in organic photovoltaic cells introducing thiophene units to TPD moieties”, The 70th Japan Society of Applied Physics Fall-Meeting, 9p-ZE-8 (Oral) Toyama University, September./2009
- [2] Ryoji Maeda, Shintaro Iwamoto, Masahide Matsuura, Hiroaki Nakamura, Hidetsugu

Ikeda, “Organic photovoltaic cells based on small-molecules introducing linear hetero-acene structures”, The 58th Japan Society of Applied Physics Spring-Meeting, 25p-BD-5 (Oral) Kanagawa Institute of Technology, March./2011

[3] Ryoji Maeda, “Development of the organic photovoltaic cells based on small molecules”, The 3rd Satellite Meeting for organic photovoltaic cells, Kanagawa Institute of Technology, March./2011

[Presentations: International Conference]

[1] Ryoji Maeda, Hiroshi Tokairin, Jun-ichi Takahashi and Yuji Yoshida, ”In-situ Measurement of Photoconductivity of Multi-layered Organic Photovoltaic Devices by Impedance Spectroscopy” Seventh International Conference on Molecular Electronics and Bio-electronics (M&BE7) ,E-08, Fukuoka International Center, March./2012

[2] Ryoji Maeda, Yoshimi Machida, Yusuke Iseki, Hiroyuki Ogo, Takeshi Gotanda, Yuji Yoshida, Hiroshi Tokairin, Tadashi Kusumoto, “High performance tandem organic photovoltaic cells based on both small molecules and conjugated polymers for each cells” 2013 MRS-Spring Meeting, B11.03, San Francisco, California, USA April/2013

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