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学位論文題目 Effects of charge carrier behavior on device performance of
organic solar cells

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Summary (Abstract) of doctoral thesis contents

Organic solar cells (OSC) are unique energy harvesting devices due to their flexibility, light weight and low fabrication cost. The performance of OSCs is determined by three parameters; the short-circuit photocurrent (J_{SC}), the open-circuit voltage (V_{OC}) and the fill factor (FF). The value of J_{SC} is related to the photo-generation process of the charge carriers. Recently, sufficiently high values of J_{SC} for practical applications have been obtained by utilizing co-deposited films, i.e., with a blend of donor (D) and acceptor (A) molecules.

On the other hand, the values of V_{OC} achieved are still too low for practical applications. Therefore, in this thesis, the author has focused on the mechanisms that determine the value of V_{OC} . The value of V_{OC} is primarily related to the energy difference (E_{DA}) between the highest occupied molecular orbital (HOMO) of the donors (D) and the lowest unoccupied molecular orbital (LUMO) of the acceptors (A). However, the observed values of V_{OC} have so far been significantly less than E_{DA} . This loss in V_{OC} is related to the energy band structure in the cell and the behavior of the charge carriers, namely, recombination and carrier transport. These processes are clarified in this thesis.

This thesis consists of five chapters.

In chapter 1, the motivation for this study and the fundamental principles of OSCs are described. The charge carrier behavior in OSCs, including carrier transport and recombination are also described, as are the impurity doping and alignment of the energy levels.

In chapter 2, the hole and electron transport in phthalocyanine (H_2Pc):fullerene (C_{60}) co-deposited films is described. The author has focused on charge carrier transport in these co-deposited films. Hole- and electron-only devices were fabricated by inserting heavily doped layers acting as ohmic contacts for holes or electrons, respectively. The carrier mobility (μ), the deep trapping lifetime (τ), and the range (L) of the charge carriers, that is, the average distance that the injected carriers can move until they are captured by the deep traps, for holes and electrons were obtained selectively by impedance spectroscopy. The dependences of μ , τ and L on the $H_2Pc:C_{60}$ ratio were also obtained. For hole-only devices, μ_h increases from 10^{-6} to 10^{-4} $cm^2 V^{-1} s^{-1}$ and τ_h decreases from 10^{-4} to 10^{-6} s as the H_2Pc ratio is increased from 50% to 83%. For electron-only devices, μ_e increases from 10^{-4} to 10^{-2} $cm^2 V^{-1} s^{-1}$ and τ_e decreases from 10^{-5} to 10^{-6} s as the C_{60} ratio is increased from

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17% to 50%. Interestingly, L_h and L_e remain constant and independent of the H₂Pc:C₆₀ ratio, with values of 0.34 and 9.4 μm , respectively, obtained.

Because of the amorphous nature of the H₂Pc:C₆₀ co-deposited films, a multiple trapping model is used to explain these results. Since holes are captured and released by shallow traps many times, μ_h is dominated by the number of shallow traps. The author proposes that the magnitude of the disorder in H₂Pc aggregates is related to the number of shallow traps. The number of shallow traps decreases with increasing H₂Pc ratio since the magnitude of disorder decreases as the H₂Pc ratio increases. Thus, μ_h increases with increasing amounts of H₂Pc. Higher μ_h shortens the time required for holes to reach the deep traps, i.e., the deep trapping lifetime (τ_h). The increase in μ_h and the decrease in τ_h cancel each other out, so L_h is independent of the H₂Pc ratio. This explanation is also valid for the observed dependences of μ_e , τ_e , and L_e on the C₆₀ ratio.

L_h and L_e are far greater than the typical thickness of co-deposited layers in organic photovoltaic cells, which is around 100 nm. There is no recombination process between holes and electrons in the hole-only and electron-only devices. Thus, the author concluded that, under conditions without recombination, electrons and holes, photo-generated in H₂Pc:C₆₀ co-deposited films, can be collected at the respective electrodes.

In chapter 3, the reasons for the loss in V_{OC} in H₂Pc/C₆₀ devices are described. In the open-circuit condition, the photo-generated charge can be described by the equilibrium between charge transfer and charge separation at the interface between the donor and acceptor layers. The energy of the photo-generated charge under open-circuit conditions is given by the charge transfer energy (E_{CT}), which is equal to E_{DA} minus the exciton binding energy. If the recombination rate increases, the observed V_{OC} becomes lower than E_{CT} . To clarify the relationship between the loss in V_{OC} and the charge recombination process, the author determined the energy loss and the charge recombination properties.

The author fabricated planar heterojunction H₂Pc/C₆₀ solar cells. Since E_{CT} is the low temperature limit of V_{OC} , the temperature dependence of V_{OC} was examined. From this, E_{CT} was determined to be 1.34 eV. The loss in V_{OC} was also determined and found to be 0.87 eV ($= E_{CT} - qV_{OC}$). In an ideal solar cell, the loss in V_{OC} is due to bimolecular recombination only. However, the measured dependence of V_{OC} on the light intensity indicates that there is both bimolecular and trap-assisted recombination in the H₂Pc/C₆₀ devices. From the results of the temperature and the light intensity dependences of V_{OC} , the energy lost due to bimolecular recombination was found to be 0.55 and that due to trap-assisted recombination was 0.32 eV.

The dependence of the recombination lifetime on the charge carrier concentration was estimated from a Cole-Cole impedance plot. The reaction order of

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the charge carrier recombination decreases as the temperature increases. A reaction order of 2 means only bimolecular recombination occurs, whereas larger numbers mean that trap-assisted recombination is also involved. The decrease in reaction order with temperature indicates that bimolecular recombination is likely to happen at higher temperatures because free charge is released from the traps.

The H₂Pc/C₆₀ devices had a large loss in V_{OC} related to trap-assisted recombination. The temperature dependence of the reaction order revealed that charge trapped at localized states was the main cause of the fast recombination. If the number of localized states can be decreased, H₂Pc/C₆₀ devices have the potential to have larger values of V_{OC} .

In chapter 4, controlling V_{OC} by impurity doping is described. The energy band structure near the interface between the donor and acceptor layers may change V_{OC} because alignment of the Fermi levels (E_F) after the different layers are brought into contact leads to a vacuum level shift near the interface and a change in E_{DA} . The author envisaged that the energy band structure could be controlled by the impurity doping, as a result of which the E_F of the organic layer could be manipulated. The author applied impurity doping to the H₂Pc/C₆₀ solar cells.

The doped H₂Pc/C₆₀ devices showed that V_{OC} decreased to 0.36 V when MoO₃ was added to the H₂Pc layer as a *p*-type dopant, whereas it increased to 0.52 V with Cs₂CO₃ as an *n*-type dopant. Energy level mapping revealed that a vacuum level shift had occurred near the donor/acceptor interface in the direction of decreasing E_{DA} with *p*-type doping and increasing E_{DA} with *n*-type doping, corresponding to the changes in V_{OC} . To investigate the effect of impurity doping near the interface, the author fabricated a number of H₂Pc/doped H₂Pc/C₆₀ tri-layer devices with different thicknesses for the thin doped H₂Pc layer. For doped H₂Pc layers from 5 to 10 nm, the V_{OC} changes gradually. The value of V_{OC} of devices with 10 nm thick doped H₂Pc is almost the same as those with 50 nm thick doped H₂Pc. The results indicate that V_{OC} is determined by the energy band structure within 10 nm of the interface between the donor and acceptor layers.

The results demonstrate that the value of V_{OC} in OSCs is determined by the energy band structure near the donor/acceptor interface. The results also showed that the energy band structure can be controlled through impurity doping and that V_{OC} can be increased by *n*-type doping. This impurity doping effect can be adapted to OSCs in general.

In chapter 5, a summary of this thesis and the conclusions drawn from it are presented. The future prospects are also given.

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This thesis can be summarized as follows.

- 1) The hole and electron ranges in the co-deposited films were estimated to be 0.34 and 9.4 μm , respectively, by impedance spectroscopy. The charge carrier ranges are far greater than the typical thickness of organic photovoltaic cells, indicating that, in the absence of charge carrier recombination, electrons and holes photogenerated in $\text{H}_2\text{Pc}:\text{C}_{60}$ co-deposited films can be collected by their respective electrodes.
- 2) The reductions in V_{OC} due to bimolecular and the trap-assisted recombination in the $\text{H}_2\text{Pc}/\text{C}_{60}$ devices were estimated to be 0.55 and 0.32 V, respectively. The temperature dependence of the reaction order revealed that charge trapped at localized states was the main cause of the fast recombination. If the number of localized states could be decreased, $\text{H}_2\text{Pc}/\text{C}_{60}$ devices have the potential for larger V_{OC} .
- 3) The value of V_{OC} can be controlled by impurity doping. The energy band structure near the donor/acceptor interface has a major effect on the value of V_{OC} . n -type doping increased V_{OC} to 0.52 V in $\text{H}_2\text{Pc}/\text{C}_{60}$ devices due to the increase in E_{DA} resulting from the vacuum level shift.

エネルギー・環境問題から有機太陽電池の高性能化に期待が寄せられている。有機太陽電池の性能は、短絡光電流(J_{sc})、開放端電圧(V_{oc})、曲線因子(FF)で表される。短絡光電流については、電荷キャリアの光生成過程が密接に関連しており、有機ドナー・アクセプター分子の共蒸着相が有力な候補として検討されている。一方で、実用化にむけては開放端電圧(V_{oc})の低さが問題視されている。開放端電圧は、原理的にはドナー分子の HOMO 準位とアクセプター分子の LUMO 準位のエネルギー差で記述されるが、観測される開放端電圧は明らかに低い値となる。本論文では、開放端電圧に焦点を当て、開放端電圧の減少メカニズムを解明するとともに、ドーピングによるエネルギー準位操作によって、技術的に開放端電圧を増大させることに成功している。

第 1 章では、本論文の目的、研究背景が述べられている。第 2 章では、フタロシアニン：フラーレン($C_{60}:H_2Pc$)共蒸着膜において、電子オンリーデバイスとホールオンリーデバイスを作製し、インピーダンス分光法によってホールと電子の移動度と寿命を別々に求め、多重トラッピングモデルに基づいてそれぞれの飛程を $0.34 \mu m$, $9.4 \mu m$ と定量的に決定した。さらに、この値は、有機太陽電池の通常膜厚の $0.1 \mu m$ よりもはるかに大きく、キャリア輸送における各種トラップサイトの存在は開放端電圧減少の要因ではないことを述べている。第 3 章では、フタロシアニン(H_2Pc)/フラーレン(C_{60})からなる 2 層型セル構造について、開放端電圧の温度依存性、光強度依存性などを評価し、 C_{60}/H_2Pc 界面のキャリア再結合が開放端電圧減少の主要原因であり、直接再結合機構によって $0.55 V$ 、トラップを介した再結合機構によって $0.32 V$ の開放端電圧減少を生じることを定量的に示している。さらに、インピーダンス分光測定による Cole-Cole プロットから求めた再結合反応次数の温度依存性から、室温でキャリアが解放されるエネルギー的に浅いトラップがトラップ再結合の主な原因であることを解明している。以上の結果から、開放端電圧を増大させるためには、 C_{60}/H_2Pc 界面を結晶化して浅いトラップの濃度を減少させる方法が有効であることを提案している。第 4 章では、同じ 2 層型セル構造について n 型ドーパント Cs_2CO_3 あるいは p 型ドーパント MoO_3 を挿入した 3 層セル構造を作製し、ドーピング効果を検証している。ドーピング層の膜厚依存性の結果から、 C_{60}/H_2Pc 界面近傍の H_2Pc 側への n 型ドーピングによって意図的に開放端電圧を増大できることを実証し、このドーピング効果は、界面近傍の $10 nm$ 膜厚領域に行うのみで発現することも明らかにしている。さらに、ドーピングによる界面の仕事関数の変化をケルビン法により実測し、ドーピングを通じて界面のエネルギー接続が操作できた結果、開放端電圧をコントロールできたことを証明している。第 5 章では、以上の結果が要約されている。

以上のように、本論文は、基礎学術的に重要な有機太陽電池の開放端電圧の減少要因を定量的に解明しただけでなく、高性能有機太陽電池へ向けた応用研究として、開放端電圧を増大できることも実証している。これらの成果は、出願者独自のアイデアを含み、基礎学術的、応用的に非常にレベルの高い研究であると判断できた。

これらの内容は、査読付き英文国際誌に、出願者が第 1 著者として 1 報がすでに掲載され、1 報がアクセプトされ、他に 1 報が投稿中である。以上のことから、審査委員会は出

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願論文が博士（理学）の授与に値すると全員一致で判断した。