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学位論文題目 *pn*-Homojunction Organic Solar Cells

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論文内容の要旨
Summary of thesis contents

Organic solar cells have been recognized as next-generation solar cells. For inorganic solar cells, *pn*-homojunctions in single inorganic semiconductors have often been utilized. In this thesis, organic solar cells based on this concept used in inorganic semiconductors are proposed. The author developed *pn*-homojunction organic solar cells, that is, *pn*-homojunctions formed in single uniform films of organic semiconductor by impurity doping. Finally, the author succeeded in fabricating organic solar cells with inorganic-like *pn*-homojunctions.

Precise *pn*-control by impurity doping is indispensable for intentionally creating a built-in potential in semiconductors. The complete *pn*-control technique has long been established for inorganic semiconductors. However, for organic semiconductors, there are only a few examples of complete *pn*-control and the formation of *pn*-homojunctions.

Previously, the doping of organic semiconductors has mainly been in the concentration range of the order of a few %. However, in order to control the built-in potential in organic solar cells, highly precise control of the doping concentration at the ppm-level is needed. So, in this study, the author attempted impurity doping at the ppm-level by using a computer monitoring system linked with a quartz crystal microbalance (QCM). The author succeeded in achieving a doping concentration of 9 ppm by volume. For doping at the ppm-level, highly purified organic semiconductors are essential. Therefore, organic semiconductors (fullerene: C₆₀, metal-free phthalocyanine: H₂Pc) having purities of 'seven-nines' (7N; 99.99999%) were used in this study. The position of the Fermi level (E_F) in organic semiconductor films is known to be very sensitive to oxygen. Therefore, during both fabrication and measurements, the cells were prevented from exposure to air by using a glove-box containing a built-in evaporation chamber and a Kelvin probe.

First of all, the author attempted the complete *pn*-control in fullerene (C₆₀) because most recent organic solar cells contain C₆₀. Since C₆₀ films behave like *n*-type semiconductors, the first attempt was to change the conduction type from *n*- to *p*-type by doping. The author found that metal oxides such as molybdenum oxide (MoO₃) and vanadium oxide (V₂O₅) act as acceptor dopants for C₆₀. This is the first report on the formation of *p*-type C₆₀. In addition, the author used Ca as a donor dopant for C₆₀, thus establishing a complete *pn*-control technique for C₆₀. This result suggests that complete *pn*-control is generally possible for other various organic semiconductors.

On the other hand, for co-deposited films, the formation of routes for photogenerated electrons and holes is essential for generating photocurrent. Recently, a method in which a

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liquid acting as a co-evaporant (polydimethylsiloxane (PDMS)) introduced into the vacuum was developed to fabricate phase-separated co-deposited films. In order to fabricate organic solar cells with inorganic-like *pn*-homojunctions, the author combined phase-separated C₆₀:H₂Pc co-deposited films and doping. Combination of the doping and the phase-separation was performed by a four-component co-evaporation technique. Finally, the author succeeded in fabricating inorganic-like *pn*-homojunction organic solar cells. Thus, electrons and holes act as minority and majority carriers, respectively. Photogenerated electrons can be extracted due to the long minority carrier diffusion length.

This thesis consists of eight chapters.

In Chapter 1, the principle of organic solar cells and the doping of organic semiconductors are described.

In Chapter 2, the experimental equipment and procedures such as the purification of organic semiconductors, the glove-box with built-in evaporation chamber, Kelvin probe measurements, multi-component co-evaporation technique, ppm-level doping technique, and photovoltaic measurements are described.

In Chapter 3, *pn*-control in C₆₀ film is described. The author adopted C₆₀ as a test material because most recent solar cells contain C₆₀. Since C₆₀ films behave like *n*-type semiconductors, the author tried first of all to change the conduction type from *n*- to *p*-type by doping. It was confirmed that molybdenum oxide (MoO₃) behaved as an acceptor. As far as the author knows, this is the first report on the formation of *p*-type C₆₀. Based on these results, general *pn*-control in other various organic semiconductors was performed.

In Chapter 4, the formation of *pn*-homojunctions in single C₆₀ films by doping is described. The position of the junction was intentionally controlled by changing the thicknesses of the MoO₃/Ca doped regions. This mechanism for the formation of *pn*-homojunctions is based on the differences in E_F caused by the controlled doping, and offers a potential method for the design and creation of built-in potentials in organic solar cells.

In Chapter 5, invertible H₂Pc/C₆₀ heterojunction cells with heavily doped organic/metal contacts are described. This is an application of the doping technique developed in Chapters 3 and 4. Ohmic contacts for metal electrodes were formed by using heavily *p*⁺- or *n*⁺-doped organic semiconductor layers. This is a similar concept to the formation of ohmic contacts in inorganic semiconductors. This heavy doping technique was used to fabricate the cells in Chapter 7.

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In Chapter 6, the fabrication of *pn*-homojunctions in co-deposited films consisting of C₆₀ and H₂Pc by doping is described.

In Chapter 7, the formation of *pn*-homojunctions in phase-separated co-deposited films of organic semiconductor is described. The carrier mobility (μ) in the film was improved by introducing a co-evaporant onto the heated substrate during film growth to produce phase-separated co-deposited films. On the other hand, carrier concentration (n) was increased by doping. Thus, the author attempted to combine doping with the introduction of a co-evaporant. This technique permitted fabrication of very thick cells up to 0.5 μm thick with very long minority carrier (electron) diffusion lengths of 250 nm.

Long minority carrier diffusion length is a key factor for photocurrent generation. In the *p*-layer, electrons and holes act as the minority and majority carriers, respectively. Even in the region without a built-in potential, photogenerated electrons can be extracted to the *n*-type region due to the large minority carrier diffusion length. On the other hand, holes with high concentration are easily extracted. Thus, organic *pn*-homojunction solar cells with a similar operating mechanism to inorganic *pn*-homojunction were successfully fabricated.

In Chapter 8, the conclusion and the future prospects are described.

In summary, the main original points of this thesis are the formation of

- 1) *p*-type C₆₀.
- 2) *pn*-homojunctions in a single C₆₀ films.
- 3) ohmic contacts at the metal/organic junctions by heavy doping.
- 4) inorganic-like *pn*-homojunctions in phase-separated co-deposited films.

The present results in this thesis will offer a new method for fabricating highly efficient organic solar cells.

Summary of the results of the doctoral thesis screening

申請者久保雅之氏は、2010年3月に山口大学大学院理工学部修士課程を修了し、同年4月より自然科学研究機構分子科学研究所において、科学技術振興機構戦略的創造研究推進事業(CREST)プロジェクト研究員として研究に従事してきた。研究内容は、有機半導体の基礎物性研究と有機薄膜太陽電池研究から成る。

有機太陽電池は、有機半導体を利用した次世代の太陽電池であり、フレキシブルな機械特性やデザイン性などの観点から実用化への研究も加速的に進められているため、その基礎学理の開拓に対しては以前にも増して注目が集まっている。

現在の主流である無機半導体を用いた太陽電池においては、完全な pn 制御（単一の半導体がドーピングのみで p 型にも n 型にもなること）が確立され、pn ホモ接合がよく用いられる。しかし、pn ホモ接合を用いた実用レベルの有機太陽電池は例がなかった。本論文において、久保氏はこのような pn ホモ接合を有する有機太陽電池の概念確立に取り組んだ。加えて、得られた新しい有機太陽電池材料に関して、基礎物性の観点から考察を行っている。

久保氏が開拓したオリジナルな点は、(1) 非常に酸化されにくく p 型化が非常に困難とされていた、有機太陽電池の基幹材料のフラーレン(C₆₀)の p 型化に、世界で初めて成功したこと、(2) 無機太陽電池と同様の、少数キャリア拡散の原理によって動作する初の有機太陽電池を作製することに成功したこと、の2点に要約できる。

具体的には、(1) ppm オーダーの極低濃度不純物ドーピングによる pn 制御が、無機半導体と同じく有機半導体でも可能と予想されるにもかかわらず、これまで実証されていなかったことから、その実証のために、有機半導体を不可避免的に p 型化してしまう酸素を 0.1 ppm 以下まで完全に排除した上、10 ppm に達する極微量体積比で不純物を共蒸着ドーピングできる技術を確認している（第2章）。(2) フラーレン(C₆₀)に対して、酸化モリブデン(MoO₃)がアクセプター性ドーパントとして働くことを発見し、p 型化することに世界で初めて成功している。なお、光電流作用スペクトルを詳細に解析し、光起電力特性からも p 型化を確認している（第3章）。(3) C₆₀ 薄膜中に pn ホモ接合を形成することに成功している（第4章）。(4) 高濃度ドーピングによって、有機/金属接合をオーミック化する方法を提案し、物性化学の観点からの考察を行っている（第5章）。(5) C₆₀ とフタロシアニンの2つの有機半導体から成る共蒸着膜に対して、ドーピング技術を応用し、250 nm もの非常に長い少数キャリア（電子）拡散距離を持つ、無機太陽電池と同様の少数キャリア拡散の原理で動作する、実用レベルの pn ホモ接合有機太陽電池を初めて作製している。この際、ケルビンプローブを用いたフェルミ準位の系統的測定により pn 接合の基本的性質を明らかにしている（第6、7章）。なお、第1章には有機半導体へのドーピングの歴史と本論文の研究を行うにあたっての基本的考え方、第8章には結論が述べられている。

以上のように、本論文では、C₆₀ の初めて p 型化に成功し、pn 制御された有機半導体の学理構築の第一歩を切り開いている。また、少数キャリア拡散を利用した pn ホモ接合有機太陽電池という、これまでにないタイプの有機太陽電池の作製に成功し、無機太陽電池と

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同様の少数キャリア拡散の原理によって、有機太陽電池を設計できることを証明しており、有機太陽電池設計の基礎学理構築に多大な寄与をしている。以上のことから、国際的にも高い水準の研究であると判定された。審査において、久保氏の研究の先見性、実験量の膨大さも伺われ、審査委員会は出願論文が博士（理学）の授与に値すると全員一致で判断した。