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学位論文題目 Design of the Energy Structures of Photovoltaic Organic
Co-deposited Films by Impurity Doping

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Organic solar cells consisting of vacuum deposited films have been actively studied due to their potential use in the fabrication of low-cost solar cells. Most recent cells use a mixture of two kinds of organic semiconductors, since cells constructed from single organic semiconductors generate little photocurrent. Co-deposition from different evaporation sources is a convenient way to mix two different organic semiconductors. Organic solar cells that include co-deposited films can generate photocurrents of significant magnitude since the efficient dissociation of excitons (bound states consisting of an electron and a hole) occurs in co-deposited films due to photoinduced electron transfer.

On the other hand, impurity-doping has been developed to precisely control the energy structures of inorganic solar cells. In the case of organic solar cells, doping techniques have not been reliably established. In particular, there has been no attempt to control the energy structures of organic co-deposited films by the use of doping.

In this thesis, the author has developed doping techniques for photovoltaic organic co-deposited films. p^+in^+ -homojunctions and an n^+p^+ -homojunction, which act as photoactive layers and as an ohmic interlayer, respectively, were fabricated in co-deposited films. A 2.4% efficient tandem organic solar cell was constructed by simply doping into co-deposited films.

This thesis consists of seven chapters.

In Chapter 1, the history and principles of organic photovoltaic cells are described.

In Chapter 2, fundamental equipment and methods are described. A co-deposited film consisting of fullerene and α -sexithiophene ($C_{60}:6T$), which exhibits a large open-circuit voltage (reaching 0.8 V) was used. Molybdenum oxide (MoO_3) was used as an acceptor dopant to create p -type films. The author found out that cesium carbonate (Cs_2CO_3) acted as a donor dopant to produce n -type C_{60} and 6T films. In order to introduce dopants into co-deposited films, the author developed a 'three component co-evaporation' technique, in which three different evaporation sources were used. Precise monitoring of the deposition rates of the dopants using a computer monitoring system enabled us to dope as low as 40 ppm by volume concentration. Direct energy-band mapping of doped junctions was achieved using a Kelvin probe.

In Chapter 3, pn -homojunctions and an n^+p^+ -homojunction, which act as photoactive layers and as an ohmic interlayer, respectively, were fabricated in single C_{60} films by simply controlling the doping concentrations of MoO_3 and Cs_2CO_3 . A tandem photovoltaic cell, whose open circuit voltage (V_{oc}) is double

that of the unit cells, was incorporated in single C_{60} films by doping alone. The energy-band diagram of the overall tandem cell was depicted based on Kelvin probe measurements for the pn - and n^+p^+ -homojunctions. The pn -homojunctions, in which an exciton is dissociated into a hole and an electron under photo-irradiation, have 130 nm-wide depletion layers. The n^+p^+ -homojunction, in which a hole and an electron neutralize each other due to recombination or tunneling, has a 20 nm-wide depletion layer. A doping technique for controlling the energy structures of single C_{60} films was established.

In Chapter 4, control of the energy structure of a C_{60} :6T co-deposited film was achieved by ppm-level doping with MoO_3 . The conduction types of C_{60} :6T films were intentionally tuned from n -type, via intrinsic, to p -type by controlling the MoO_3 doping concentration. The potential profiles of MoO_3 -doped C_{60} :6T films mapped using a Kelvin probe enabled us to confirm the transition of the energy structure. The results confirmed that MoO_3 acts as an acceptor dopant in the case of C_{60} :6T co-deposited films.

In Chapter 5, tuning of the barrier parameters of n -type Schottky junctions formed in C_{60} :6T co-deposited films was achieved by ppm-level control of Cs_2CO_3 doping. The carrier concentration of electrons, as evaluated by capacitance measurements, showed a clear proportional relationship to the overall doping concentration of Cs_2CO_3 . The results confirmed that Cs_2CO_3 acts as a donor dopant for the C_{60} :6T co-deposited films. In addition, the doping efficiency was found to be around 0.15.

In Chapter 6, since the pn -properties of the C_{60} :6T co-deposited films could be completely controlled by doping with MoO_3 and Cs_2CO_3 , organic solar cells were designed in the C_{60} :6T films by use of these doping techniques. The author fabricated a series of fundamental junctions, that is, p - and n -type Schottky junctions, pn , p^+in^+ , and ohmic n^+p^+ homojunctions, and ohmic junctions between metal electrodes and heavily-doped p^+ and n^+ layers. Based on these doping techniques, a tandem organic solar cell was formed in a C_{60} :6T film by connecting two photoactive p^+in^+ -homojunctions via a heavily doped n^+p^+ -ohmic interlayer. The value of V_{oc} and the conversion efficiency of the tandem cell reached 1.69 V and 2.4%, respectively.

In Chapter 7, the conclusion of this thesis is described. The author constructed doping techniques for designing the energy structures of photovoltaic C_{60} :6T co-deposited films. Complete control of the pn -properties of photovoltaic C_{60} :6T co-deposited films was achieved by doping with MoO_3 and Cs_2CO_3 . A series of fundamental junctions, that is, p - and n -type Schottky junctions, pn , p^+in^+ , and ohmic n^+p^+ homojunctions, and ohmic junctions between metal electrodes and heavily-doped p^+ and n^+ layers, were fabricated. A 2.4% efficient tandem organic solar cell was built in a C_{60} :6T co-deposited

film fabricated by doping only. Energy-band mapping and capacitance measurements strongly assisted in the clarification of the operating mechanisms of the doped junctions.

The introduction of direct doping into bulk co-deposited films can provide the following improvements in the design of organic solar cells. (i) A built-in electric field can be constructed directly in the co-deposited region where the generation and transport of photocarriers occurs. (ii) A reduction of the bulk resistance of co-deposited films by doping can enable the growth of co-deposited films that are sufficiently thick (e.g. 1 μm) to absorb the whole of the incident solar light and to convert it to a photocurrent. Therefore, these doping techniques could significantly help in the development of an efficient organic solar cell.

有機太陽電池は、低価格、フレキシブル、印刷による作製ができる、等の利点を持つため、精力的に研究されている。低分子の有機半導体を用いる太陽電池においては励起子を分離して実用的な光電流量を得るために、電子移動によって励起子を電子とホールの自由キャリアに分離できるエネルギー関係を持つ2種の異なった有機半導体を、共蒸着（同時蒸着）によって混合して作製するのが主流となっている。

一方、無機半導体の太陽電池においては、不純物ドーピングによるpn制御（伝導タイプ制御）が確立されているが、有機半導体の太陽電池においては、pn制御によるセル設計方法が確立されておらず、特に、2つの有機半導体から成る共蒸着膜に対するpn制御とそのセル応用は、研究例が皆無であったため、石山氏は本研究でそれらの課題に挑戦している。

本論文では、共蒸着膜を1つの有機半導体とみなして不純物ドーピングによるpn制御を行い、セルの内蔵電界の設計を行い、ドーピングのみによって共蒸着膜中にタンデムセルを作り込み、効率2.4%を得ている。

具体的には、(1) 3元蒸着によって、共蒸着膜に、ppm オーダーの低濃度で不純物ドーピングを行う技術を確立している（第2章）。(2) フラーレン(C_{60})とチオフェン誘導体（sexithiophene: 6T）の共蒸着膜(C_{60} :6T)に、アクセプター性ドーパントとして働く MoO_3 のドーピングを行い、p型化することに成功している（第4章）。(3) ドナー性ドーパントとして働く Cs_2CO_3 を発見し、 C_{60} :6T 共蒸着膜にドーピングを行い、n型化することに成功している（第5章）。(4) C_{60} 単独薄膜中に、ドーピングのみによって、2つのpnホモ接合を連結した、タンデムセルを作り込むことに成功している（第3章）。(5) C_{60} :6T 共蒸着膜中に、光電流を発生する p^+in^+ 接合（+は高濃度ドーピングを意味）と、有機/有機トンネルオーミック接合となる n^+p^+ 接合を、ドーピングのみで作成してタンデムセルを作製し、効率2.4%を得ている（第6章）。(6) ケルビン振動容量法によって、上記のセル全体のエネルギー構造を実測で描く方法を提案している（第3、5、6章）。なお、第1章は有機太陽電池の歴史と原理、第7章は結論が述べられている。

以上のように、本論文では、有機半導体の共蒸着膜のpn制御を初めて確立し、これまでにないタイプの有機太陽電池を不純物ドーピングのみによって作製することに成功しており、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、石山氏の研究に対する深い理解や、粘り強い取り組みが窺われた。公開発表も内容、質疑応答ともにきちんとしており、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。