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(別紙様式 2)
(Separate Form 2)

論文の要旨
Summary (Abstract) of doctoral thesis contents

The potential low-cost of organic semiconductor devices has resulted in a great deal of attention being paid to this type of semiconductor. In the case of organic photovoltaic cells, co-deposited films, i.e., blends of two types of organic semiconductor, have been widely studied. In addition, to design an energetic structure, impurity doping is the standard technique.

Furthermore, the standard method for separately and simultaneously determining the carrier concentration (N) and mobility (μ) in doped inorganic semiconductors is by making Hall effect measurements. However, the use of this method for doped organic single crystals has not, so far, been reported.

In this doctoral thesis, the author has focused on the development of a precise impurity doping technique at the ppm level both for organic thin films and organic single crystals. The carrier concentration per unit volume (N, cm^{-3}) and the mobility (μ) of doped organic single crystals were successfully determined using the Hall effect for the first time. Moreover, the performance of organic photovoltaic cells was enhanced by directly doping co-deposited films even with extremely low doping concentrations of 1 ppm.

This thesis consists of six chapters.

In chapter 1, the background to the impurity doping of both inorganic and organic semiconductors and the motivation for carrying out the research work described in this thesis are presented.

In chapter 2, the experimental equipment and methods are described. Rubrene single crystals possessing band-like transport properties were employed for the Hall effect measurements. Co-deposited films of fullerene and α-sexithiophene (C_{60}:6T) were used for the organic photovoltaic cells. Iron chloride ($FeCl_3$) and cesium carbonate (Cs_2CO_3) were used for the accepter and donor dopants, respectively. Doped organic semiconductors were fabricated using a ‘multi-component co-evaporation’ technique. The deposition rates of the dopants were monitored using a quartz crystal microbalance equipped with a computer monitoring system. These rates were controlled using rotating shutters with aperture ratios of 1/10, 1/100, and 1/1000, which enabled us to control the doping concentration to as low as 1 ppm.

In chapter 3, the Hall effect measurements made on the doped organic single crystals is described. Also, the first successful achievement of the fabrication of a doped homoepitaxial single crystal layer on rubrene single crystal by an ultra-slow co-deposition technique is described. The minimum deposition rate for 1 ppm doping with $FeCl_3$ was 10^{-9} nm s^{-1}. A

systematic study of both the hole concentration per unit volume (N, cm^{-3}) and the Hall mobility (μ_H) of $FeCl_3$-doped homoepitaxial rubrene single crystal was carried out using Hall effect measurements. With 100 ppm doping, N = 2.6 x 10^{17} cm^{-3} and μ_H = 1.4 $cm^2V^{-1}s^{-1}$ were obtained. It was found that (i) the doping efficiency, i.e., the ionization rate of the acceptor dopant, of the rubrene single crystal (24%) was higher than that of a rubrene vacuum deposited film (1.2%), which can be attributed to the lower concentration of hole traps and that (ii) there was a decrease in μ_H from 4.6 to 0.13 $cm^2V^{-1}s^{-1}$ as the doping concentration was increased from 10 to 1000 ppm, which can be attributed to scattering effects due to lattice disturbances. These results are a first example of Hall effect measurements made on doped organic single crystals.

In chapter 4, the field-effect mobility of doped organic single crystals are described. FET mobility (μ_{FET}) can be regarded as the drift mobility (μ_D), which is dominated by carrier traps. The drift mobility (μ_D) was about two-orders of magnitude less than the Hall mobility (μ_H). Since holes captured by traps cannot move under the influence of the Lorentz force, μ_H contains no contribution from the trapped holes. So, we concluded that the lower μ_D values can be attributed to the effect of hole traps formed by lattice disturbances, which decrease the velocity of the holes by capturing them. The activation energy of the hole traps was determined to be 0.37 eV by measuring the temperature dependence of μ_D.

In chapter 5, the effects of impurity doping in simple n^+p-homojunction organic photovoltaic cells are described. Here, + means heavily doped. The n^+p-homojunctions were formed in C_{60}:6T co-deposited films with acceptor ($FeCl_3$) and donor (Cs_2CO_3) dopants. The doping concentration of $FeCl_3$ in the *p*-layer was varied from 1 to 1000 ppm. The doping effects can be divided into three regions. Firstly, from 0 to 10 ppm, the fill factor (FF) increased due to the appearance of majority carriers (holes). Secondly, from 10 to 100 ppm, the photocurrent density (J_{sc}) increased due to an increase in the built-in potential, i.e., the formation of an n^+p-homojunction. Thirdly, above 100 ppm, FF and J_{sc} decreased due to the decrease in hole mobility and depletion layer width, respectively. Thus, we confirmed that the photovoltaic cell performance could be enhanced by the extremely low doping concentration of 1 ppm.

In chapter 6, the conclusion to this thesis and prospects for the future are presented. The following summarizes the achievements made in this work.

1) ppm-level doped homoepitaxial rubrene single crystal was successfully fabricated by means of an ultra-slow co-deposition technique with a deposition rate as low as 10^{-9} nm s^{-1}.
2) Hall effect in doped rubrene single crystal was systematically measured for the first time.
3) A relatively high doping efficiency, reaching 24%, and a decrease in μ_H due to scattering effects owing to lattice disturbances were observed in the doped rubrene single crystal.
4) Enhancement of the photovoltaic performance with an extremely low doping concentration of 1 ppm was confirmed.

The author believes that the work described in this thesis will lead to the following future developments.

1) The detailed doping mechanism in doped organic single crystals, such as the state of the dopants, the doping induced lattice disturbances, such as vacancies, interstitials, etc., will be clarified.
2) New types of organic device using doped organic single crystals will be fabricated.

(別紙様式 3)
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博士論文審査結果の要旨

Summary of the results of the doctoral thesis screening

有機太陽電池に代表される有機半導体デバイスにおいて、不純物ドーピングは必要不可欠な方法となっている。しかし、1 ppm に達する極微量ドーピングの効果については、研究例がほとんどなかった。本博士論文では、ppm ドーピングした有機単結晶のホール効果測定に世界で初めて成功し、ppm ドーピングした有機薄膜太陽電池の光起電力特性が受ける影響の系統的な解明に成功した。

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、アクセプター(Fe_2Cl_6)の蒸着速度を 10^{-9} nm/s まで超低速にする技術による ppm ドーピング法、ホール効果によるドーピング有機単結晶のキャリア濃度・移動度の測定法、等の実験手法が述べられている。第３章では、ルブレン有機単結晶上にホモエピタキシャル成長させたルブレン単結晶膜に、Fe_2Cl_6 アクセプターを 1 から 1,000 ppm ドーピングし、キャリア濃度と移動度を、ホール効果によって系統的に測定し、有機単結晶のドーピング効率（イオン化率）が 24%で、アモルファス膜の 1.2%に比べ格段に大きい結果を述べている。第４章では、上記のドーピングしたルブレン単結晶の電界効果(FET)移動度の測定から､ホール移動度は散乱により FET 移動度はトラップによって支配されていること、および、ドーピング効率はドーピングに伴うトラップ形成を抑制することでさらに向上できる可能性を述べている。第５章では、pn ホモ接合を持つ有機薄膜太陽電池において、1 ppm の極微量ドーピングから特性に影響が現れること、すなわち、p 層のアクセプター濃度 0〜10 ppm では多数キャリアの発生により曲線因子が増大し、10〜100 ppm では内蔵電界の増大により光電流が増大し、100〜1,000 ppm ではキャリア移動度の減少により曲線因子が減少することを述べている。第６章では、簡潔なまとめと今後の展望が述べられている。

以上のように、本論文は、有機半導体への ppm ドーピング、ドーピング有機単結晶という、これまでにない新分野を開拓している。

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報が掲載されている。以上のことから、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。