論文 / 著書情報
Article / Book Information

題目(和文)	液晶性有機半導体とアクセプタ分子の混合系における薄膜形成と電子デバイス応用に関する研究
Title(English)	Study on film fabrication of liquid crystalline organic semiconductors and acceptor molecules with their device applications
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種別(和文)	論文要旨
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（博士課程）
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論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	電気電子 電気電子	系 コース	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of	（ 工学 ）
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

Liquid crystalline organic semiconductors are expected to be applied to organic transistors because uniform thin films can be easily formed over a large area in a solution process by forming films via the liquid crystal phase. However, organic field effect transistors (OFETs) have some problems, such as the difficulty in developing materials for N-channel operation and the high contact resistance between the metal and semiconductor. Although there have been significant developments in P-channel OFETs with mobility exceeding 10 $cm^2\ V^{-1}\ s^{-1}$, research on N-channel OFETs has not progressed as much, mainly due to the trapping of electrons by water and oxygen molecules in the atmosphere. In order to ensure stable operation in air, N-channel OFET materials must possess a deep lowest unoccupied molecular orbital (LUMO) level, which is responsible for electron transport. As for contact resistance, the device characteristics are limited by the contact resistance in the case of the higher contact resistance. OFETs have higher contact resistance than inorganic transistors. To solve these problems, we have improved and modulated the characteristics of OFETs by combining liquid crystalline organic semiconductors and acceptor molecules.

In chapter 3, the single crystals of phenyl-benzothienobenzothiophene derivatives (Ph-BTBT-n, n=10, 8, 6) and fluorinated 7,7,8,8-tetracyanoquinodimethane derivative (F_4-TCNQ) charge-transfer complexes (CTCs) were prepared by recrystallization in mixed solvents of acetonitrile and chlorobenzene, and their crystal structures and transistor operation were evaluated. All of the CTCs have similar crystal structures, which are one-dimensional crystal structures consisting of a BTBT core and a TCNQ core in a π-stacked configuration. FET measurements of a single crystal of (Ph-BTBT-10)(F_4-TCNQ) showed N-channel transistor operation with a mobility of 0.04 $cm^2\ V^{-1}\ s^{-1}$. As described above, this chapter clarified the crystal structure of (Ph-BTBT-n)(F_4-TCNQ) single crystals and concluded that (Ph-BTBT-n)(F_4-TCNQ) can be applied as N-channel OFETs.

In chapter 4, I proposed a new fabrication process of CTC thin films by thermal diffusion and evaluated the thin films. X-ray diffraction, absorption spectra, and photoemission yields spectroscopy showed formation of (C_{10}-BTBT)(F_4-TCNQ) and (Ph-BTBT-10)(F_4-TCNQ) by thermal diffusion of stacked these thin films in a short time at a low temperature of 80 °C and 120 °C for 30 seconds, respectively. These OFETs exhibited air-stable N-channel operation with mobility in the 10^{-4} -10^{-3} $cm^2\ V^{-1}\ s^{-1}$. Based on photoelectron yield

spectroscopy and absorption spectra, the LUMO level of (Ph-BTBT-10)(F_4-TCNQ) fabricated by thermal diffusion was estimated to be -5.6 eV, indicating that the injection and stable transport of electrons in air are possible. (Ph-BTBT-10)(F_4-TCNQ) thin films were more likely to form using Ph-BTBT-10 monolayer crystal structures than bilayer crystal structures. It is suggested that the disordered alkyl chains of the Ph-BTBT-10 monolayer crystal structure derived from the structure of the liquid crystal phase facilitated the thermal diffusion of F_4-TCNQ molecules. F_4-TCNQ layer can be stacked not only by vacuum deposition but also by solution process. By depositing F_4-TCNQ molecules on Ph-BTBT-10 layer by blade coating and thermal annealing, (Ph-BTBT-10)(F_4-TCNQ) was formed to realize an N-channel transistor. It is concluded that the process of preparing CTC thin films using thermal diffusion is one of the important development approaches for N-channel organic transistors.

In chapter 5, I aim to improve the characteristics of P-channel OFETs based on liquid crystalline organic semiconductor Ph-BTBT-10 by doping acceptors. In the case of bottom-gate top-contact FETs, the contact resistance was reduced from 3 kΩcm to 1.2 kΩcm by depositing F_4-TCNQ molecules at the interface between Ph-BTBT-10 and source-drain electrodes. Contact resistance was further reduced to 0.9 kΩcm by thermal annealing. This is because F_4-TCNQ molecules diffuse into the Ph-BTBT-10 layer just below the electrode, (Ph-BTBT-10)(F_4-TCNQ), which acts as a dopant for Ph-BTBT-10, is formed, and the access resistance is reduced. In the case of bottom-gate bottom-contact OFETs, the threshold voltage (V_{th}) could be controlled to -0.5 ~ -2 V by changing the concentration of fluorinated tetracyanonaphtho-quinodimethane (F_6-TCNNQ) up to 10^{-5}-10^{-1}. This is due to the positive shift of the V_{th} caused by the generation of carriers by doping. It is concluded that acceptor doping plays an important role in reducing contact resistance and V_{th} in organic transistors.

Through these studies, I conclude that combining liquid crystalline organic semiconductor and accepter molecules realizes to develop N-channel OFETs, reduce contact resistance and control threshold voltage of OFETs. In this study, I developed CTC thin films with (C_{10}-BTBT)(F_4-TCNQ) and (Ph-BTBT-10)(F_4-TCNQ), and I expect to develop materials with high electrical properties by using various materials in the future. In addition, by patterning acceptor molecules on liquid crystalline organic semiconductors, N-channel and P-channel OFETs can be formed on the same substrate, which is expected to be applied to complementary circuits.