学位論文の要旨

Abstract of Thesis

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学位論文題目 Title of Thesis（学位論文題目が英語の場合は和訳を付記）

Study on transistor application of new phenacene-type molecules: characterization of molecules, device fabrication and operation properties
(新しいフェナセン型分子のトランジスタへの応用に関する研究：分子のキャラクタリゼーション，デバイス作製ならびに動作特性)

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Field-effect transistor (FET) is an essential component of modern electronics. Recently, the field-effect transistors (FETs) using organic molecules have attracted much attention because of ubiquitous / sustainable features such as flexibility, light-weight and shock resistance, as well as such as ease of design and low-cost / low-energy consumption in fabrication process [1-4]. During the past thirty years, much effort has been devoted to development of high-performance organic FETs [4-7]. Namely, synthesizing new organic molecules suitable for active layers of FETs and optimizing device structure have been attempted together with the innovation of fabrication processes. The strong π-π interaction between molecules is one of the most important factors for the improvement of channel transport in FET device. Therefore, molecules that can form the close packing in the crystal lattice must be synthesized and applied to active layers of FETs. Moreover, the reduction of trap states and contact resistance are also significant to realize high-performance FET. Actually, the detailed investigation of trap states in channel region of FET must be conducted to clarify the factors suppressing FET properties [8-10]. From these viewpoints, the following research subjects are explored in this doctoral study.

The author applied newly synthesized phenacene derivatives to the active layers of FETs. The molecules are dibenzo[n]phenacenes (DBnPs: n = 5 – 7), which can be recognized as 'acene-phenacene hybrid molecule'. The single crystals of DBnPs are employed for the active layers of FETs. Among the above molecules, DB6P showed the excellent FET properties with the averaged μ value of 2.0(7) $cm^2 V^{-1} s^{-1}$. In particular, the DB6P single-crystal FET showed an ideal Shockley-type transfer curve with the high effective field-effect mobility μ_{eff} [11]. The concept of design of the molecules is that the FET properties will be improved because acene-phenacene hybrid molecules would provide the strong π-π interaction owing to extended benzene network and it would possess high energy level of highest occupied molecular orbital (HOMO) in comparison with those of phenacene molecules. Through this study, C_{2h}-symmetrical DB6P showed higher FET performance than C_{2v}-symmetrical DB5P and DB7P molecules, because C_{2h}-symmetrical molecules can probably form the close packing in the crystal lattice. These results are described in chapter 4 of doctoral thesis.

Moreover, thin-film FETs using new phenacene derivatives as active layers are described in chapter 6. The newly synthesized molecules of alkyl-phenyl[n]phenacenes (PhCn'-[n]phenacenes: n = 4 – 6) accompany alkyl substituent, either decyl or tetradecyl group. The concept of design of the molecules is that the introduction of alkyl and phenyl groups to phenacene cores would lead to close packing *via* fastener effect to provide large transfer integral between molecules. As a consequence, the high μ value (= 1.66 $cm^2 V^{-1} s^{-1}$) was recorded in 3-decyl-10-phenyl[5]phenacene (PhC10-PIC). Thus,

the introduction of alkyl and phenyl groups could lead to the high-performance FETs. The structural and electronic properties of molecules synthesized are also demonstrated in chapters 4 and 6.

In chapter 5, the author reports the trap states in channel region of DBnPs and the charge transfer integrals between molecules to quantitatively elucidate the origins governing FET characteristics. Here, the temperature dependence of μ and conductance G of DBnPs were fully investigated, and the multiple trap and release (MTR) model [9] and Lang's method [12] were employed to obtain the information on trap states. The Lang's method showed that trap states were located in narrower region near HOMO level for DB6P in comparison with DB5P and DB7P. Furthermore, the theoretical calculation with the atomic coordinates determined from single-crystal X-ray diffractions was conducted to evaluate the transfer integrals between molecules, indicating larger transfer integrals in DB6P than other molecules; the theoretically evaluated μ was also higher, which was consistent with the fact that DB6P provided high μ value. These results indicate that DB6P forms the close packing, and that narrow distribution of trap states leads to superior FET performance; it is natural to point out that the narrow (shallow) distribution would be directly associated with low $|V_{th}|$.

In chapter 7, the FET properties of phenacene molecules were revisited using a new indicator μ_{eff}, which was evaluated by reconstructing the observed transfer curve to an ideal Shockley-type one [11]. The transfer curves of FETs sometimes provided very concave behavior (non-linear behavior) which showed apparently high μ value. Such a concave behavior originates from the high $|V_{th}|$; other types of transfer curves which are deviated from Shockley-type transfer curve are also observed frequently. The FETs exhibiting the transfer characteristics deviated from ideal Shockley-type transfer curve are not recognized as 'superior FET device'. Namely, the FET must provide both high μ and low $|V_{th}|$ values. From this viewpoint, the values of μ_{eff} of phenacene molecules that the FET properties have been reported during a past decade were re-evaluated, demonstrating that [8]phenacene and [9]phenacene molecules as active layers showed great potential in single-crystal FETs, and that alkyl-substituted picene was promising for use as active layers in thin-film FETs with high-k gate dielectrics. In addition, the tendency that the μ increases against number of benzene rings (n) was also confirmed in the plot of μ_{eff} – n.

In this doctoral thesis, the author has attempted to seek the strategy for realizing high-performance FET devices through (1) employment of new phenacene derivatives which were designed based on the concept that the strong π-π overlap and fastener effect should be involved, as well as (2) quantitative understanding of origins dominating FET characteristics. From the perspectives, we found some criterion for selecting molecules for active layers of FETs. Moreover, it has been found that revisiting the results reported as 'superior FET performance' is of significance. Admittedly, even after re-examination of FET properties, some phenacene and phenacene derivatives were still promising for active layers.

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