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（博士課程）
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論 文 要 旨

THESIS SUMMARY

専攻： Department of	Electronics and Applied Physics 専攻	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of （Engineering）
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要旨（英文800語程度）
Thesis Summary (approx.800 English Words)

In this thesis, several serials of mono-alkyl chain smectic liquid crystalline semiconductors were synthesized to clarify three questions: (1) does the bilayer crystal structures widely exist?, (2) what is the essential requirements for its formation?, (3) does its formation always boost solution-processed OFETs mobility?, which arose from the molecular design strategy based on Ph-BTBT-C10 proposed by our group previously.

In Chapter 1, firstly, a short introduction of organic field-effect transistors (OFETs) was descripted, following by smectic liquid crystal. Next, the history of OFET materials with liquid crystallinity but without utilization of it was summarized. After that, a method named liquid crystal temperature spin-coating method which utilizing liquid crystallinity for fabricating uniform polycrystalline thin films used for OFETs was presented, following by its generalization to mono-alkyl chain liquid crystalline semiconductors featuring highly ordered SmE phase. Then, several proposed molecular packing modes of SmE phase and its additional benefits for thin film fabrication were elucidated. At last, we introduced our group newly proposed amazing mono-alkyl chain liquid crystal semiconductor, Ph-BTBT-C10, and focus on the phenomenon of the dramatic FET mobility enhancement caused by formation of a bilayer crystal structure through phase transition from a monolayer crystal structure thermally induced. Based on that, the research motivation and purpose of present work was proposed.
In Chapter 2, the experimental methods were introduced in detail. The chemical structures were characterized by 1H-NMR and MS spectrum. The mesophase behaviors were investigated by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction (XRD). The formation of bilayer crystal structure was studied by XRD and the FET performance was evaluated by two source measurement units.

In Chapter 3, two serials of mono-alkyl π-conjugated semiconductor materials based on oligomer systems and fused-ring systems were synthesized to clarify the 1st question. In oligomer systems, three kinds of mono-alkyl oligomer derivatives, i.e., Ph-BTP-C18, Ph-TTP-C18 and QTP-C10, were synthesized. After characterization by DSC, POM and XRD, it found that both Ph-TTP-C18 and QTP-C10 exhibited single highly ordered SmE phase, while Ph-BTP-C18 was just a crystal. Later XRD study on their bulk film samples before and after thermal annealing (TA) showed that all of them could form the bilayer crystal structure. Similar clarification process was applied to fused-ring systems of two serials of mono-alkyl derivatives, i.e., ones based on PAHs of Ph-NAP-C8, Ph-PAT-C12 and Ph-BPT-C12; the others based on S-PAHs of BTBT-C8, Ph-BDT-C14 and Ph-NDT-C14. Similar results were obtained, i.e., all of them could form bilayer crystal structures. Thus, we could conclude that the bilayer crystal structure was not a particular case for Ph-BTBT-C10, and it might be widespread existence in mono-alkyl π-conjugated semiconductor materials.

Chapter 4 was to clarify the 2nd question. Two possible effect factors on the formation of bilayer crystal structures, i.e., the alkyl chain effect and the π-conjugated core effect, was supposed. For the alkyl chain effect, two subparts were investigated, i.e., the length of alkyl chain and the number of alkyl chain. For the first one, a serial of Ph-TTP-Cn ($6 \le n \le 18$) with different lengths of alkyl chain were synthesized. Similar characterization process for mesophase properties and formation of bilayer crystal structure were executed. It found that all of them exhibited single highly ordered SmE phase and the bilayer crystal structure could be formed when the length of alkyl chain $n \ge 10$. For the later one, a serial of C8-BTBT-Cn ($0 \le n \le 8$) with different lengths of oppositional terminal alkyl chain were synthesized. It found that ONLY when the lengths of oppositional terminal alkyl chain equal to 0, the bilayer crystal structure could be formed.

For the π-conjugated core effect, three kinds of fused-ring compounds with different π-conjugated cores but same length of mono-alkyl chains, i.e., Ph-NAP-C8, Ph-PAT-C8 and Ph-BPT-C8, were synthesized. It found that when the size of π-conjugated core was enlarged, the bilayer crystal structure trended to deform. Thus, it is possible to clarify the 2nd question as the bilayer crystal structure could ONLY form in mono-alkyl chain π-conjugated materials and also a delicate balance between the lengths of alkyl chain and the size of π-conjugated core should be carefully optimized.

Chapter 5 was to clarify the 3rd question. Two serials of mono-alkyl smectic liquid crystal semiconductors featuring bilayer crystal structure based on oligomer systems and fused-ring systems were selected to study their FET performance before and after TA. In the oligomer systems, Ph-TTP-Cn ($10 \leq n \leq 18$) was selected. XRD characterization of polycrystalline thin film fabricated by liquid crystal temperature spin-coating method was done to re-confirm the existence of phase transition from the monolayer to bilayer crystal. Indeed, all as-coated thin films adopted a monolayer crystal structure and could transform to a bilayer crystal structure after TA. FET mobility of OFET devices fabricated with those spin-coated polycrystalline thin films was enhanced by about one order of magnitude when the formation of bilayer crystal structure by phase transition from the monolayer crystal structure thermally induced. In the fused-ring systems, three kinds of materials, Ph-PAT-Cn, Ph-BPT-C12 and Ph-BDT-Cn, were selected. Similar results were obtained. Thus, it is possible to clarify the 3rd question as the FET mobility was always enhanced when the formation of the bilayer crystal structures by phase transition from the monolayer crystal structures.

In conclusion, the phenomenon of "OFET mobility enhanced by phase transition from monolayer crystal structure to bilayer crystal structure" is NOT a particular case for Ph-BTBT-C10, and would be general for solution-processed OFET devices fabricated with mono-alkyl SmE OFET materials featuring bilayer crystal structure, providing us with a new approach for OFET devices with high FET performance.