Extended Abstracts of the 2005 International Conference on Solid State Devices and Materials, Kobe, 2005, pp.972-973

F-9-1 (Invited)

Organic Thin-film Transistors Based on n-type Organic Semiconductors

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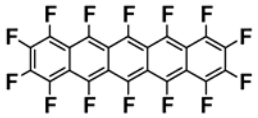
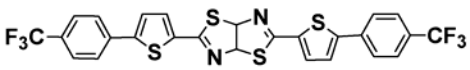
1. Introduction

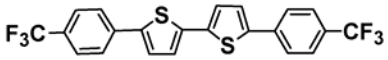
Remarkable progress in the development of thin-film transistors (TFTs) based on organic semiconductors has been demonstrated over the past 10 years. Good performance by several p-types has been reported for organic TFTs (OTFTs). OTFTs based on pentacene and sexithiophene have demonstrated especially high field effect mobility over 1cm^2/Vs and a current on/off ratio over 10^5, which are superior to that of amorphous silicon. However, there have been no high performance n-type OTFTs comparable to pentacene TFTs. There is a particular need to develop high performance n-type OTFTs because they enable complementary circuits and



1: Perfluoropentacene



2: Thiazolothiazole derivative



3: Bithiophene derivative

Fig. 1 Molecular structures of new n-type organic semiconductors.

an ambipolar OTFT. In this paper, we present new n-type organic semiconductors and discuss their OTFT performance.

2. Perfluorination of pentacene

As fluorine is the most electronegative element, fluorination would be an effective way to introduce a p-type character to an aromatic molecule. Perfluorination of aromatic molecules would lower their lowest unoccupied molecular orbital (LUMO) level, which is effective for electron injection from the electrode, and would stabilize the anionic forms of the molecule and allow them to efficiently transport negative charges. Perfluoropentacene (Fig. 1) has been developed for new n-type organic semiconductors through the perflurorination of pentacene and has demonstrated a low LUMO level. X-ray diffraction patterns for perfluoropentacene thin film formed by vacuum evaporation have revealed diffraction peaks up to the third order, indicating that the molecules are standing perpendicular to the substrate, which is favorable to charge transport in OTFTs.

OTFTs were fabricated on a highly-doped Si wafer with a 200-nm-thick thermal oxide. Perfluoropentacene thin film (50 nm) was formed on the Si wafer at 50℃ by vacuum evaporation. Source and drain electrodes were also formed through a shadow mask by vacuum evaporation using gold on the perfluoropentacene film. The channel length was 100 μm and the channel width was 1000 μm. Electrical measurements on the OTFTs were carried out in a high vacuum chamber immediately after they were fabricated without exposure to air. Figure 2 plots the characteristics of drain current vs. drain voltage at various gate voltages. When the gate

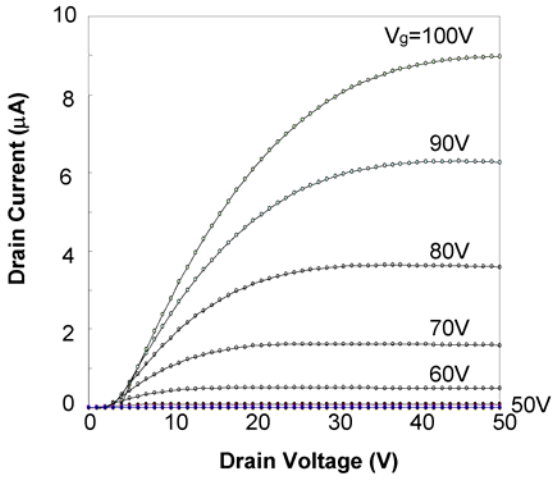


Fig. 2 I_d-V_d characteristics of an OTFT based on perfluoropentacne.

electrode was biased positively with respect to the grounded source electrode, remarkable drain current and saturation were observed, indicating that perfluoropentacene is an n-type semiconductor. The threshold voltage was –50 V. The field effect mobility calculated from the device characteristics was found to be 0.1cm^2/Vs and the current on/off ratio was 10^5, which is almost comparable to that of a conventional pentacene TFT fabricated on the same substrate.

A complementary MOS inverter was demonstrated using a combination of perfluoropentacene with pentacene on an SiO_2/Si substrate, and good performance was obtained. Furthermore, an ambipolar TFT was also successfully demonstrated in a mutilayer of perfluoropentacence and pentacene thin films.

3. Trifluoromethylphenyl-substituted heterocyclic molecules

Substituting an electron-withdrawing aromatic group instead of fluorine to a molecule would also create an n-type semiconductor. The trifluoromethylphenyl group was substituted to the heterocyclic molecules such as bithiophene and thiazolothiazole derivatives as shown in Fig. 1. These molecules were planar, the same as perfluoropentacene, which is favorable for intermolecular stacking. In fact, the X-ray diffraction patterns for bithiophene derivative and thiazolothiazole derivative thin films showed reflections up to the second or third order and the d-spacing was comparable to the molecular length, indicating that the molecules were almost standing on the substrate. The electrochemical measurements revealed that these molecules had low LUMO levels. The thiazolothiazole derivative, which had a smaller HOMO-LUMO gap, had an especially lower LUMO level of 2.93 eV.

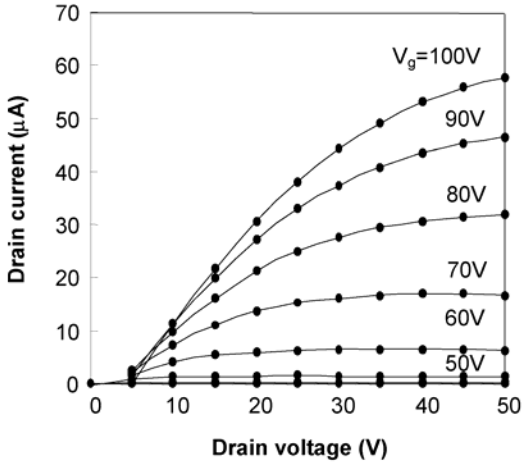


Fig. 3 I_d-V_d characteristics of an OTFT based on thiazolothiazole derivative.

The OTFTs using these new semiconductors were fabricated on an SiO_2/Si substrate at 50℃. Drain current vs. drain voltage characteristics in OTFTs based on the thiazolothiazole derivative exhibited n-channel behavior and the threshold voltage was 60 V (Fig. 3). A significantly high mobility of 0.3 cm^2/Vs was obtained and the current on/off ratio was 1 x 10^6. The bithiophene derivative also gave a high mobility of 0.18 cm^2/Vs and a current on/off ratio of 3 x 10^5. These mobilities are comparable to the highest value (~0.6cm^2/Vs) reported in a perylene derivative.

4. Conclusion

The new n-type organic semiconductors have been developed by perfluorination and trifluoromethylphenyl-substitution to the planar aromatic molecules. The performance of OTFTs using the new n-type semiconductors is summarized in Table 1. The mobility and current on/off ratio are almost comparable to those of the excellent p-type semiconductors.

Table 1 Performance of OTFTs based on new n-type organic semiconductors.

Organic Semicon.	Mobility (cm^2/Vs)	On/Off ratio	Threshold (V)
1	0.11	1x10^5	50
2	0.3	1x10^6	60
3	0.18	3x10^5	76

Acknowledgements

The author would like to thank Professor Y. Yamashita and S. Ando of the Tokyo Institute of Technology and Professor T. Suzuki and Dr. Y. Sakamoto of the Institute for Molecular Science for materials syntheses and their characterizations.

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