



Materials and devices with applications in high-end organic transistors



J. Takeya*, T. Uemura, K. Sakai, Y. Okada

Institute for Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

ARTICLE INFO

Available online 5 November 2013

Keywords:

Organic semiconductor
Organic transistors
Organic thin-film transistor
Organic single-crystal transistor
Solution crystallization
Printed electronics
Flexible electronics

ABSTRACT

The development of functional materials typically benefits from an understanding of the microscopic mechanisms by which those materials operate. To accelerate the development of organic semiconductor devices with industrial applications in flexible and printed electronics, it is essential to elucidate the mechanisms of charge transport associated with molecular-scale charge transfer. In this study, we employed Hall effect measurements to differentiate coherent band transport from site-to-site hopping. The results of tests using several different molecular systems as the active semiconductor layers demonstrate that high-mobility charge transport in recently-developed solution-crystallized organic transistors is the result of a band-like mechanism. These materials, which have the potential to be organic transistors exhibiting the highest speeds ever obtained, are significantly different from the conventional lower-mobility organic semiconductors with incoherent hopping-like transport mechanisms which were studied in the previous century. They may be categorized as “high-end” organic semiconductors, characterized by their coherent electronic states and high values of mobility which are close to or greater than $10 \text{ cm}^2/\text{Vs}$.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Various materials may be crystallized to fabricate high-mobility organic field-effect transistors (OFETs) and their charge transport properties have been investigated through temperature dependent four-terminal conductivity, Hall effect and pressure dependency measurements. These materials include conventional polyacenes, such as pentacene and rubrene, recently developed high-mobility heteroacenes such as dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene (DNNT) and 2,9-didecyl-dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene (C10-DNNT), 2,7-dialkyl[1]benzothieno[3,2-b]benzothiophenes and the V-shaped molecules such as 3,9-didecyl-dinaphtho[2,3-b:2',3'-d]thiophene (C10-DNT-VW) which were recently synthesized for use in high-mobility printed semiconductor devices.

In general, the results of Hall effect measurements tell us that charge transport in devices which exhibit excellent room temperature mobility in the range of $5\text{--}10 \text{ cm}^2/\text{Vs}$ is governed by band-transport mechanisms which result when electronic states are spatially extended over the molecule. In contrast, a peculiar electronic state is found in pentacene devices with charge dynamics midway between band transport and hopping transport, characterized by a Hall effect signal approximately half that of the fully extended electronic systems.

The effects of pressure on carrier mobility in various OFETs have also been investigated as a means of establishing variations in charge transport as a function of structural changes. The carrier mobility has been found to increase rapidly, at rates of about 20%/GPa for rubrene, 50%/GPa for pentacene and 80%/GPa for DNNT; all of which are greater than

the rates observed with conventional inorganic semiconductors. It is also noteworthy that the specific molecular structure of a compound can cause unusual pressure effects; compression of the rubrene crystal is restricted by the presence of four phenyl groups on the periphery of the central tetracene framework, thus the pressure effect is suppressed above 0.6 GPa [1], in contrast to the behavior of pentacene and DNNT which contain simple linear π -conjugated systems.

2. Charge coherence in high-performance organic transistors

Organic semiconductors which consist of assemblies of weakly van-der-Waals bonded, π -conjugated molecular units can serve as mechanically soft platforms capable of moderate electronic charge transport. The weak bonding energies of these compounds allow the use of simple fabrication processes such as solution casting to form bendable electronic devices on plastic substrates near room temperature. As such, these compounds have attracted considerable attention with the expectation that they may serve in the next generation semiconductor industry as flexible and printable electronics. However, since both weak intermolecular bonding and ready molecular displacement are deleterious to intermolecular charge transfer, it is not an easy task to simultaneously achieve high charge transport efficiency and good mechanical flexibility. There is therefore an urgent need to understand the changes in the fundamental electronic states as the materials are subjected to the intrinsic competition between these two effects. In this regard, we have identified a dephasing effect on the electronic charge caused by thermal fluctuation of the molecules, detecting a direct response of charge flow under external magnetic fields due to fundamental coupling with the electron phase in pentacene field-effect

* Corresponding author.

transistors (the most popular devices in terms of anticipated practical applications). These results indicate an inherent constraint on charge flow in organic semiconductors, and suggest that thermal fluctuations should be minimized in the design of organic molecules intended for use in higher-performance transistors.

Studies on charge transport in organic semiconductors date back to the 1970's, when the possibilities of both band transport of diffusive electrons (described by wave numbers or k values) and consecutive hopping between electronic states self-localized in the molecules (described by their positions or r values) were already being discussed [2]. Experimentally, however, the limited charge carrier densities obtainable with photo-doping at that point in time often led to significant difficulty in achieving the intrinsic electronic states in which the effects of the charge-trapping sites are most pronounced. In addition, the cross-over between the two most extreme cases, in which either k or r adequately describes the states, had not been detected experimentally, since measurement processes capable of quantitatively following one-electron phase coherence were not available.

With the development of OFETs, much higher carrier densities up to 10^{20} cm^{-3} can be achieved in organic semiconductors with high mobility, so that studies on intrinsic electronic states are accelerated with the measurement of the steady current associated with electrostatically doped charges, in the event that interface trap states are not dominant. In particular, the development of organic single-crystal transistors has contributed to the detection of genuine charge transport distinct from the influence of grain boundaries. Furthermore, recent measurements of the Hall effect in such systems have clearly shown that free-electron-like diffusive transport is realized in several high-mobility organic semiconductors, including rubrene and DNTT. The Hall voltage in these substances results from the off-diagonal component (σ_{xy}) of the transport coefficients according to the linear response theory, based on the coupling of the electronic state described by k and the vector potential A in the cross term of the kinetic Hamiltonian. The experimental results for rubrene and DNTT transistors evidently satisfy the free-electron relationship $R_H = 1/Q$, where Q is the charge density estimated from the dielectric capacitance of the insulating gate layers. The proposed band-like transport in rubrene single crystals is reinforced by the results of other experimental studies, such as those involving infrared spectroscopy and angle-resolved photo-emission spectroscopy [1,3].

At present, however, an important question which remains unanswered is the existence and the nature of intermediate electronic states capable of bridging the self-localized polaron and diffusive band-like transport. This situation therefore resembles the historical arguments concerning the existence of the Mott transition in disordered systems [4]. The work presented herein demonstrates that pentacene-based OFETs appear to be a missing link, since these electronic carriers do couple with magnetic fields to generate a finite Hall voltage but the magnitude of this voltage is considerably less than the free-electron value at room temperature. Since the Hall effect is a manifestation of the coupling of electrons to a magnetic field through their plane-wave phase, the results observed in the case of pentacene show that the one-electron phase coherence of these materials is weaker than that of the band-transport systems. Intriguingly, the deviation of R_H from the free-electron value is greater at higher temperatures, indicating that thermal fluctuations of the pentacene molecules are responsible for this effect. These observations cannot be adequately explained by the simple scenario of conventional electron-phonon scattering and are therefore attributed to a significant effect resulting from fluctuating molecular displacements.

In this paper, we report on the Hall effect in both pentacene single crystals and thin-film transistors. The pentacene single crystal transistors were fabricated using the same method described in our previous reports on rubrene single crystal transistors [4,5]. Fig. 1(a) shows an optical view of a pentacene single crystal transistor. The channel between the voltage-probing electrodes has dimensions of width (W), length (L)

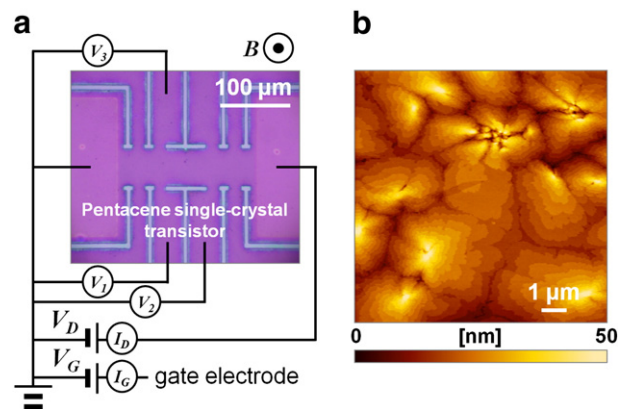


Fig. 1. Samples of pentacene field-effect transistors used during experimental trials. (a) Optical view of a pentacene single-crystal transistor for Hall effect measurements, including a schematic diagram showing the measurement of voltages at different positions in the channel. (b) AFM image of a pentacene thin-film transistor.

and distance (l) of 60, 200 and 80 μm , respectively. In the thin-film devices, essentially the same channel dimensions were generated by laser etching. Fig. 1(b) shows an atomic-force microscope (AFM) image of the thin-film device, which demonstrates that a typical polycrystalline pentacene thin film with the average grain size in the order of several μm is fabricated to form the semiconductor channel. We used commercial AFM equipment by SEIKO Instruments, and a tungsten probe is used for tapping-mode measurement.

Fig. 2(a) and (b) presents the plots of the inverse Hall coefficient ($1/R_H$) and σ_{\square} as a function of gate voltage (V_G) for both the pentacene single crystal and thin-film device at 280 K. We developed a home-made system for the measurement based on a cryostat by Oxford Instruments. The magnetic field was swept in the range of ± 10 T. Electric-field induced transport characteristics are measured using Keithley Semiconductor Parameter Analyzers. In both plots, σ_{\square} is seen to increase with decreasing values of V_G due to hole accumulation in the channel. We defined the field effect mobility (μ_{FET}) resulting from the four-terminal measurement as equal to $1/C \cdot \partial\sigma_{\square}/\partial V_G$, such that μ_{FET} was estimated to be $1.5 \text{ cm}^2/\text{Vs}$ in both the single crystal and the thin-film device. Similarly, $1/R_H$ is observed to increase with decreasing V_G , due to charge accumulation. This result demonstrates that the value of $1/R_H$ is proportional to the value of the carrier density while the sign of $1/R_H$ indicates that the carriers are holes. The black broken line portrays the carrier density (Q) calculated as the product of the capacitance (C) and V_G . The variable V_{th} is defined as the threshold voltage derived from the extrapolation of the plot of $1/R_H$ vs. V_G , giving the threshold of highly-mobile carriers and disregarding trapped charge. Note that the value of $1/R_H$ does not coincide with that of Q , such that the value of $1/R_H$ is approximately twice that of Q in the single crystal device. This result was reproduced quantitatively in three single crystal devices fabricated on different SAM-treated substrates. Similarly, the value of $1/R_H$ is twice Q in the thin-film devices, which appears to be consistent with the results of Takamatsu et al. [6,7].

These results already contrast those obtained during previous experimental work with rubrene and DNTT transistors, in which the values of $1/R_H$ and Q very precisely agree with one another, indicating that free-electron-like diffusive band-transport is occurring. Since the finite positive Hall voltage of pentacene transistors studied in the prior work is half that measured in the DNTT transistors, their electronic state must involve some degree of coherence over the entire molecule, even though the phase coherence is weaker than that of the above free-electron-like systems. As examples of more incoherent electronic systems, more highly disordered systems such as a-Si transistors typically show even smaller Hall voltages, about one-tenth of the free-electron values, and with anomalous signs [8–10]. For convenience, we introduce here a factor that describes the extent of the coupling

Download English Version:

<https://daneshyari.com/en/article/1665625>

Download Persian Version:

<https://daneshyari.com/article/1665625>

[Daneshyari.com](https://daneshyari.com)