Invited Review

Materials and Device Properties of High-mobility Organic Transistors

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(Received Oct. 24, 2014)

Organic transistors are MOS-type field-effect transistors in which an organic semiconductor is used as the active layer. Some organic semiconducting compounds are highly soluble in certain solvents, so that it becomes possible to form a semiconductor thin film by solution coating. Thus, there are considerable expectations for innovative industrial applications, in which low-cost, large-area devices can be produced on plastic films using printing technology. In this report, I introduce the physics of carrier transport in an intermolecularly delocalized electronic state, which is a key factor for realizing high-performance organic transistors. I also describe prospects for the industrial application of printable single-crystal organic semiconductors with mobilities exceeding 10 cm²/V·s.

Keywords: Organic semiconductor, Organic transistor, Organic thin-film transistor, Organic single-crystal transistor, Solution crystallization

1. Introduction

Organic field effect transistors (OFETs), in which an organic semiconductor is used as the active layer, are considerably expected for practical industrial applications. Their advantage is that a wide variety of low-cost, large-area devices can be manufactured in small quantities using printing technology, as some organic semiconducting compounds are highly soluble in common solvents. With inorganic semiconductors, high-temperature processes in the range of 300-1000°C are necessary. In contrast, with organic semiconductors, low-temperatures processes in the range of room temperature to a few hundred degrees Celsius can be used. Another benefit of organic semiconductors is that they offer excellent mechanical flexibility. Thus, research and development are being carried out toward the realization of new devices such as flexible displays and plastic electronic tags, by fabricating organic semiconductor circuits on plastic substrates.

Generally, the binding energy between atoms in inorganic semiconductors is several electron volts, whereas in low-molecular-weight organic semiconductors, the energy associated with molecular aggregation is more than one order of magnitude smaller. In the absence of a chemical change, they sublime at a few hundred degrees even under ordinary pressures. This makes it easy to deposit organic semiconductors on flexible substrates such as plastics. In particular, coating with π-conjugated molecules dissolved in an organic solvent at around room temperature offers excellent productivity, so this is directly linked to the development of low-cost semiconductor devices. The term "printed electronics" is also used for this process, and it is attracting a lot of attention from a wide range of industry sectors, including the electronics and printing industries.

Organic semiconductors composed of molecules with low molecular weights form soft solids due to weak intermolecular forces between generally a single type of π-conjugated molecules. This allows them to be prepared by simple methods at temperatures close to room temperature and provides them with mechanical flexibility. This is in contrast with inorganic semiconductors as typified by silicon, in which strong covalent bonds hold the atoms together, forming a hard solid. Presently, these unique semiconductors made of organic materials are drawing a lot of attention even from industry. However, the carrier transport in a "soft solid" is not well understood at present. Recently, progress has been made in the development of organic semiconductor transistors with high mobilities of the order of 10 cm²/V·s. Since this is one order of magnitude higher than the value of about 1 cm²/V·s for conventional organic semiconductors, it raises expectations for next-generation semiconductor devices. In this report, we focus on high-mobility organic semiconductors, and investigate the mechanisms for achieving high-mobility carrier transport, utilizing the Hall effect, which is produced by the action of a magnetic field on a current.

In the case of silicon, which is strongly covalent, electrons are delocalized among the orbitals of covalent bonds as shown in Fig. 1a, and band conduction takes place. The energy gain for transitions between valence and conduction bands is given by the band gap of the semiconductor.

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through delocalization is several electron volts, which is the same as the binding energy. The effective mass of electrons is a few tenths of the mass of free electrons, depending upon the bandwidth. In an organic semiconductor, however, where molecules are held together by weak intermolecular forces, the degree of orbital overlap is much smaller, and is more strongly affected by molecular vibrations even at room temperature. Such vibrations have a detrimental effect on carrier transport (Fig. 1b). In other words, although the softness of the material makes it flexible and allows easy low-temperature fabrication, it also makes it difficult to produce devices that exhibit both high mobility and high performance. In order to achieve this, it is first necessary to understand microscopic carrier transport.

2. Hall measurements on high-mobility organic semiconductor transistors

2.1 High-mobility organic transistors

An organic transistor has a structure similar to that shown in Fig. 2. Carriers are injected by applying an electric field to the gate insulator film. When a gate voltage \( V_G \) is applied between the gate electrode and the organic semiconductor active layer, an electric field appears in the gate insulating layer, which gives rise to a build-up of charges on the surface of the organic semiconductor facing the gate electrode. Since the carriers injected into the organic semiconductor can move, if a drain voltage \( V_D \) is applied between the source and drain electrodes, a drain current \( I_D \) is produced when \( V_G \) is applied. The charge per unit area \( Q \) that is introduced into the organic semiconductor is given by \( Q = C(V_G - V_a) \), where \( C \) is the capacitance of the gate insulator film and \( V_a \) represents the threshold voltage. The conductivity \( \sigma \) can then be expressed as \( \sigma = Q\mu = ne\mu \), where \( n \) is the electron density, \( e \) is the elementary charge, and \( \mu \) is the mobility. Accordingly, the mobility \( \mu \) can be determined from the change in \( \sigma \) with \( V_G \).

Before the year 2000, the reported mobility values for organic transistors (organic FETs) were not very high, the largest being about 1 cm²/Vs for a pentacene (Fig. 3a) polycrystalline thin film that was prepared by vacuum evaporation. In many polycrystalline thin films, the mobility showed a tendency to decrease with temperature. For this reason, the mobility was often considered in terms of a modified version of the Marcus equation represented by

\[
\mu = \frac{2}\hbar \frac{e^2}{k}\frac{\lambda^4}{\lambda + t} \exp\left(-\frac{\lambda}{kT}\right),
\]

where \( \hbar \) is the Planck constant, \( k \) is the Boltzmann constant, \( e \) is the elementary charge, \( \lambda \) is the intermolecular distance, \( T \) is the temperature, \( t \) is the intermolecular charge-transfer integral, and \( \lambda \) is the reorganization energy. For example, when the carriers are holes, conduction is thought to occur by hopping transport. In this model, the holes become localized at \( \pi \)-conjugated molecules, causing them to become cations, and the holes sequentially jump to neighboring molecules. Thus, a neighboring molecule must be oxidized in each hopping step. The amount of energy required is obtained by subtracting the energy associated with the charge-transfer integral \( t \) due to overlap of neighboring molecular orbitals, from the reorganization energy \( \lambda \) due to the molecular deformation. If this energy is positive, the temperature change is thermal-activation type.

In the present century, numerous organic transistors with high mobility have been developed, mainly using conjugated organic molecular compounds.
mobilities exceeding 1 cm²/Vs have been reported, starting with single-crystal organic semiconductor transistors and including transistors based on newly synthesized organic semiconductors. For a rubrene (Fig.3b) single-crystal transistor, the mobility was found to increase at temperatures lower than room temperature, which led to the suggestion that carrier transport was occurring through band conduction, in which carriers are delocalized between molecules. It has been argued for some time that in bulk ultra-high-purity organic semiconductor crystals, photo-excited carriers undergo band conduction, based on the temperature dependence of the mobility determined by time-of-flight measurements. There has been increased interest in clarifying the transport mechanism for carriers in actual high-mobility transistors, which accumulate at the interface between the organic semiconductor and the gate insulator.

2.2 Hall measurements on OFETs

Despite the fact that the Hall coefficient is one of the most basic transport properties, a considerable amount of time passed before it was measured for organic transistors. In inorganic transistors such as those made from silicon, the carrier concentration and mobility have been accurately determined using Hall measurements, and important information concerning the conduction mechanism has been obtained for amorphous materials. Therefore, the development of effective measurement methods for organic FETs has been strongly desired. In past organic thin film transistors, the conductivity was several orders of magnitude smaller than that for inorganic semiconductors and the impedance was at least 1 MΩ. As a result, satisfactory detection sensitivity could not be achieved, making measurements difficult.

In 2005, for the first time, Hall measurements using a high-mobility rubrene single-crystal FET were achieved. The measurement precision has subsequently been improved, and the technique has since been applied to a variety of high-mobility organic semiconductors. In the present report, results will be presented for a range of high-mobility organic semiconductors used in organic FETs, for which Hall measurements have already been carried out. The carrier transport mechanism will then be discussed. In addition to pentacene and rubrene, these semiconductors are dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene (DNTT), 2,7-diocyl[1]benzothiophene (C8-BTBT), and 2,7-dioctyl[1]benzothiophene (C8-BTBT), which were recently synthesized by Takimiya et al. (Ref. 5).

The Hall effect occurs due to the Lorentz force exerted by a magnetic field on a continuous flow of carriers (current); therefore, the presence of delocalized carriers is assumed. Thus, when the dominant carrier transport mechanism is hopping conduction, it is extremely difficult to measure the electromotive force due to the Hall effect. On a microscopic level, the electromotive force occurs along the direction perpendicular to both the current J and magnetic field B, based on the primary term in the Hamiltonian, in which the wavenumber operator k for an electron with an effective mass of m* and the vector potential A are coupled, \( \frac{1}{2m^*} (eA - cA)^2 \), which represents the motion of a charged particle. The Hall coefficient R_H, which is determined from the transverse voltage (Hall voltage) V_H, using the expression R_H = V_H / I_D B, is linked to the charge per unit area q by the relation R_H = (1/ne) under conditions of low inelastic scattering, when the carriers are free-electron-like and the state defined by the wavenumber k is realized. On the other hand, in the case of hopping conduction in which electrons propagate by a discontinuous tunneling process, the only influence of the magnetic field is to interfere with the hopping pathways. Therefore, V_H is extremely small, if it can be measured at all. In fact, for low-mobility amorphous silicon, V_H is only 1/10 of that for free-electron-like transport.

Thius, it is possible to investigate the carrier conduction mechanism using Hall measurements, and such measurements were carried out for various high-mobility organic semiconductors.

In Fig. 4, an experimental setup for high-sensitivity Hall measurements is shown. An organic FET is first fabricated by patterning a single-crystal or polycrystalline thin film organic semiconductor on a gate insulating layer such as silicon dioxide. In addition to the source and drain electrodes for current flow, four electrodes are formed for accessing the central section of the channel so that the Hall voltage and four-terminal conductivity can be measured simultaneously. A current is passed between the source and drain while a magnetic field is applied perpendicular to the conduction channel, and the Hall voltage and the potential drop in the channel are measured.
3. Hall measurements on organic single-crystal rubrene FET

Since no grain boundaries exist in a single-crystal FET, the intrinsic carrier transport coefficient for the organic semiconductor layer can be measured. Since a rubrene single-crystal FET was the first organic FET for which Hall measurements were carried out, we will begin by describing the results for this device.\(^{10,13}\)

A single crystal of rubrene was prepared by the physical vapor transport (PVT) method. This is a simple and commonly-used method in which a temperature gradient is set up in a tubular furnace, the raw material is sublimed in the high-temperature section and transported to the low-temperature section by a flow of argon gas, and the organic molecules then become crystallized. This method produces a crystal with the structure shown in Fig. 5, where the molecules are arranged two-dimensionally on the surface. The rubrene molecules constitute a conjugated electron system, in which the \(\pi\) electrons in the four central benzene rings become delocalized, and the molecular plane is perpendicular to the crystal surface. Accordingly, when the plate is viewed from the top, the molecular planes appear as straight lines running in directions inclined approximately 30° to the \(b\)-axis. Intermolecular electron transfer occurs due to the \(\pi\) orbitals that extend parallel to the surface. This in-plane conductivity offers advantages because the interface with the gate insulator can be formed along this plane. In this study, a single-crystal transistor was fabricated by selecting a thin rubrene single crystal (thickness of 1 \(\mu\)m or less) and laminating it onto the \(SiO_2\) gate insulator by electrostatic attraction.

Fig. 6 shows the results of the Hall measurements. The reciprocal of the Hall coefficient \(1/R_H\) is plotted with respect to the gate voltage \(V_G\), and it is compared with the charge per unit area \(Q'\) estimated from the capacitance of the gate insulating layer and \(V_G\). It can be seen that the two sets of values are in good agreement, and increase with negative gate voltage. This implies that holes injected by the field effect do not become localized in the molecules but are widely distributed among the molecules. From the dependence of the four-terminal conductivity on the gate voltage, also shown in Fig. 6, the mobility in this device was about 8 cm\(^2\)/Vs. The high degree of carrier delocalization implies that the transistor undergoes band-type conduction at room temperature. Based on the results of Hall measurements, Podzorov et al. also reported band-type conductivity for a rubrene single-crystal transistor at room temperature.\(^{11}\)

Carrier delocalization in rubrene single-crystal FETs was later also identified using other experimental methods. Li et al. reported low-energy Drude-type conductivity based on the results of light absorption measurements.\(^{15}\) Recently, Machida et al. carried out angle-resolved photoelectron spectroscopy of rubrene single crystals, and observed a clear band dispersion.\(^{20}\)

In addition, the intermolecular electron density in rubrene was directly determined by high-intensity X-ray diffraction. As shown in Fig. 7, the presence of electrons 'shared' among rubrene molecules was actually confirmed. Thus, it can be concluded that an intermolecularly delocalized electronic state is realized in the rubrene crystal, which gives rise to the high carrier mobility.

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Journal of the Imaging Society of Japan Vol. 53 No. 6 (2014)
4. Transistors based on new organic semiconductors DNTT and C$_8$-BTBT

Since a free-electron-like Hall effect was identified in the rubrene single-crystal FET, it is necessary to next investigate whether this is also the case for other high-mobility organic semiconductors. Takimiya et al. developed high-mobility organic semiconductor materials such as DNTT, C$_8$-BTBT and C$_{10}$-DNTT, whose structures are shown in Fig. 3. They found that high mobilities of about 3, 4 and 8 cm$^2$/Vs, respectively, could be obtained in polycrystalline thin-film transistors$^{5-7}$. Since these compounds are less easily oxidized than pentacene and are stable in air, there is considerable interest in their practical application. For C$_8$-BTBT and C$_{10}$-DNTT, single-crystal transistors were also fabricated by solution coating and the maximum mobility values obtained were 6 and 11 cm$^2$/Vs, respectively$^{16,17}$. Furthermore, although preparation of polycrystalline rubrene thin films is difficult, both single-crystal and polycrystalline films of DNTT, C$_8$-BTBT and C$_{10}$-DNTT can be prepared, allowing a comparison of the conduction mechanism in each type of film.

4.1 DNTT single-crystal FET prepared by PVT method

A single-crystal DNTT FET fabricated using the same PVT method used for rubrene was found to exhibit a typical mobility of about 3 cm$^2$/Vs$^{21}$. When prepared by other methods, a maximum mobility of 8 cm$^2$/Vs was obtained$^{22}$. Fig. 8 shows the results of Hall measurements for the FET fabricated using the PVT method. The measurements were carried out using the method described in Section 2. As was the case for rubrene, $1/R_H$ and $Q$ are in extremely good agreement, so it can be concluded that the carriers are delocalized. This result suggests that rubrene is not the only organic semiconductor that exhibits band-type conduction, and that an intermolecularly delocalized electronic state is more commonly obtained in high-mobility organic semiconductors$^{14}$.

4.2 C$_8$-BTBT and C$_{10}$-DNTT high-mobility single-crystal FETs prepared by solution crystallization method

Single-crystal FETs based on C$_8$-BTBT and C$_{10}$-DNTT were prepared by a method in which a crystal is precipitated on a substrate from a solution$^{14,15}$. In the case of C$_8$-BTBT, a room-temperature process was possible because its solubility is sufficiently high$^{20-22}$. As shown in Fig. 9a, the crystal is precipitated by tilting the substrate, retaining liquid droplets at the end of the liquid-holding structure, and drying for several minutes$^{20}$. Unlike a normal spin-coating method, this method has the advantage that it can produce thin films containing a large domain, in which the direction of crystal growth is controlled. On the other hand, since sufficient room-temperature solubility cannot be obtained for C$_{10}$-DNTT, the process was carried out at about 100°C. As shown in Fig. 9b, a large domain can also be formed by precipitating a crystal with the use of a hotplate while controlling the direction. Transistors fabricated by this method have good properties as shown in Fig. 10 and 11. In addition, the maximum mobility obtained was more than 10 cm$^2$/Vs, and mobility comparable to that of amorphous oxide can be achieved by the solution process at about 100°C. Thus, it is expected that this method will have practical industrial applications$^{15}$.

4.3 DNTT and C$_8$-BTBT polycrystalline TFTs prepared by solution crystallization method

Hall measurements were carried out for a polycrystalline
DNTT TFT using the same method, and the results were compared with those for the single-crystal FET. In a polycrystalline material, the presence of high-resistance grain boundaries is expected to have a detrimental effect on the FET characteristics. The measured Hall electromotive force is the sum of electronegative forces associated with each crystal grain, even in the polycrystalline case, if the crystal grains are electrically connected. Therefore, it is expected that a Hall coefficient similar to that for a single-crystal organic semiconductor would be obtained if the carriers behave in a free-electron-like manner. Accordingly, the transport mechanism of carriers can be investigated in more detail than before by clarifying the electronic state inside the crystal grains.

Fig. 12 shows the results of Hall measurements for a DNTT polycrystalline transistor. Again, there is extremely good agreement between $1/R_s$ and $Q$. Thus, even for a DNTT polycrystalline thin film prepared by vacuum evaporation, the microscopic arrangement of DNTT molecules was sufficiently regular and the carriers were delocalized inside the grains. The measured sample mobility was about 1 cm$^2$/Vs, which is lower than that for single-crystal DNTT.

In Fig. 13a, the temperature dependence of the mobility is compared with that for the single-crystal FET. For the polycrystalline sample, it was found that the mobility decreases with temperature. In the past, this would have been attributed to hopping conduction. However, the results of the Hall measurements indicate that band-type conduction occurs inside the crystal grains. Therefore, the mechanism is different from simple hopping transport, with carrier localization inside molecules, as expressed in equation (1). In fact, in the DNTT single-crystal case, very little decrease in the mobility is observed, at least above 200 K. The same results were obtained, as shown in Fig. 13b, for C$_8$-BTBT prepared by vapor deposition. This suggests that this is the general case for high-mobility polycrystalline organic thin films.

Regardless of whether band-type conduction occurs inside the crystal grains, the decrease in mobility at low temperature for the polycrystalline transistor may be the effect of shallow traps at grain boundaries. These are associated with disorders and defects at the grain boundaries, and their effect becomes more prominent as the temperature decreases. Thus, by combining Hall and four-terminal conductivity measurements, it has become possible to qualitatively separate the contributions to electron transport from inside crystal grains and grain boundaries. Thus, carrier transport in the high-mobility polycrystalline thin films can be understood in more detail.

5. Pentacene single-crystal and polycrystalline FETs

Finally, Hall measurements were performed for pentacene single-crystal and polycrystalline FETs. The single-crystal device was fabricated by laminating vapor-deposited thin crystals, and the polycrystalline device was produced by vacuum evaporation. Typical values were obtained for the mobility, namely about 2 cm$^2$/Vs for the single-crystal device, and about 1 cm$^2$/Vs for the polycrystalline device.

Although all of the high-mobility organic semiconductors described thus far exhibited a free-electron-like Hall effect, Fig. 14 shows that for the Pentacene FETs, no agreement was found between $1/R_s$ and $Q$. Similar results were also obtained by Sekitani et al. for a polycrystalline pentacene thin film.
Since the measurement precision in Fig. 14 is the same as that for the other samples, this difference must reflect the intrinsic properties of pentacene. From Fig. 14, \( \frac{1}{R_H} > C \frac{|V_G - V_d|}{V_G} \) for both single-crystal and polycrystal transistors, whereas the relationship \( \frac{1}{R_H} < C \frac{|V_G - V_d|}{V_G} \) was reported by Podzorov et al. for a rubrene single-crystal FET at temperatures lower than room temperature\(^{11}\).

The number of high-conductivity carriers that contribute to the Hall effect (i.e., not localized in traps) is not larger than the number of carriers estimated from the capacitance and gate voltage. Therefore, the results indicate that the microscopic state of the carriers accumulated on pentacene deviates from the free-electron-like picture. Interestingly, the room-temperature values for the carrier coherence factor \( \alpha \), which is the ratio of \( \frac{1}{R_H} \) to the slope of \( C \frac{|V_G - V_d|}{V_G} \), were approximately the same for five pentacene samples with different mobilities, regardless of whether they were single crystals or polycrystalline. This suggests that \( \alpha \) is determined by microscopic factors inside the molecules or crystal grains, and is not affected by trap levels at grain boundaries or elsewhere.

If we recall that the Hall effect is due to the coherence of electron wave functions, the results for pentacene FETs imply that carrier coherence is not maintained over sufficient distances. Since there is no sample dependence, it is likely that this is due to molecule-specific factors rather than extrinsic factors such as disorders. Fig. 15 shows that \( \alpha \) increases with decreasing temperature. This suggests that molecular vibrations, which increase with temperature, strongly influence the carrier coherence. As described in the Introduction, molecular vibrations are large in organic semiconductors, even at room temperature, so this effect may become too large to ignore. In fact, it was theoretically shown by Troisi that when the effect of molecular vibrations is large, carriers may become localized\(^{24}\).

It would be of interest to examine the reasons why, among all the semiconductor systems for which Hall measurements have been carried out to date, the effect of molecular vibrations is large only in the case of pentacene. The results may serve as guidelines for the design of organic semiconductors that exhibit a high mobility at room temperature. Comparing the molecules shown in Fig. 3, it can be seen that the shape of the pentacene molecule has the highest symmetry. It is therefore plausible that it could easily vibrate along its long-axis direction even under the influence of intermolecular forces from neighboring molecules. An attempt was made to carry out Hall measurements for C\(_60\), which is a molecule with even higher symmetry than pentacene, but the Hall coefficient was so small that the measurements were not possible. Based on the measurement sensitivity limit, this would imply \( \alpha < 0.1 \). Therefore, the effect of molecular vibrations for C\(_60\) is considered to be larger than for pentacene. In the future, experiments should be carried out to verify the above hypothesis for different molecules\(^{15}\).

6. Summary and prospects

A high-precision method for carrying out Hall measurements even for FETs based on organic semiconductors was developed, and measurements were carried out on different high-mobility organic FETs. The results highlighted the fact that Hall measurements are a powerful tool for investigating the essential mechanisms of carrier transport in single-crystal and polycrystalline thin films of organic semiconductors, as has
long been the case for inorganic semiconductors. That is, the
number of carriers accumulated by the field effect can be
accurately determined as a quantity proportional to the
capacitance. Therefore, essential information concerning car-
rier coherence can be obtained by comparing the reciprocals of
the Hall coefficients.

In many organic semiconductors such as rubrene, DNTT,
C8-BTBT, and C10-DNTT, which show mobilities of several
cm²/Vs or more, the Hall coefficient was similar to that for
expected using the typical free-electron-like model. Thus, the
high-mobility carrier transport in these systems was clarified
to be based on a band mechanism due to an intermolecularly
delocalized electronic state. On the other hand, this was
different to the case for pentacene FETs, for which the
electronic state was more strongly affected by molecular
vibrations at room temperature. This lead to a reduction in
electron coherence, and the Hall electromotive force that is
produced by coupling with the magnetic field is weaker than
that for a fully coherent free-electron-like state. Thus, suitable
design of organic molecules may be an effective approach for
developing high-mobility organic semiconductors. In the
future, a more quantitative investigation should be carried out
in combination with theoretical considerations, and further
verification is also necessary in other systems.

Lately, new organic semiconductors are being developed at
an impressive rate. Significant progress has also been made
with regard to solution processes, which take maximum
advantage of the fact that organic semiconductors can be
fabricated by coating at temperatures near room temperature.
Organic FETs exhibiting a mobility exceeding 10 cm²/Vs can
now be produced by the coating method. In the future, the
potential industrial applications of high-mobility organic
semiconductors will increase. We believe that understanding
carrier transport in such semiconductors will promote further
material development and the expansion of research into the
electronic properties of interfacial two-dimensional electron
systems.

References

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He is a Professor in Graduate School of Frontier Sciences at the University of Tokyo since 2013. He got his Ph. D. at the same university in 2001 when he was a research scientist in Central Research Institute of Electric Power Industry from 1991. He was an Associate Professor in Graduate School of Science at Osaka University from 2006 and was a Professor in Institute of Scientific and Industrial Research at the same university from 2010 before moving to the current position. His research interests lie in the area of material science and device physics of organic electronics.