Hall Effect of Quasi-Hole Gas in Organic Single-Crystal Transistors

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Hall effect is detected in organic field-effect transistors, using appropriately shaped rubrene (C22H20) single crystals. It turned out that inverse Hall coefficient, having a positive sign, is close to the amount of electric-field induced charge upon the hole accumulation. The presence of the normal Hall effect means that the electromagnetic character of the surface charge is not of hopping carriers but resembles that of a two-dimensional hole-gas system.1

KEYWORDS: organic field-effect transistor, OFET, Hall effect, rubrene, single-crystal FET

In quest of next-generation materials for fundamental electronic components, organic semiconductors are attractive due to their simple fabrication processes, low production cost, capability of low energy synthesis, and mechanical flexibility as well as sensitivity to light.1,2) Although the organic semiconductors have been proven to be available for the elemental circuit components, represented by field-effect transistors (FETs), the full performance of the materials would be significantly reduced in broadly studied polymeric or polycrystalline thin-film devices by extrinsic effects such as those caused by grain boundaries.3) Indeed, recently developed single-crystal organic FETs (OFETs) have demonstrated that the intrinsic FET performances are superior to those reported for thin-film OFETs; the FET mobility \(\mu_{\text{FET}}\) reaches as high as 20 cm\(^2\)/Vs, and the subthreshold swing is comparable to that of normal single-crystal silicon FETs for an aromatic molecular compound, rubrene.4,5) The fact that a molecularly flat surface free from dangling bonds is easily grown for the organic single crystals may be partially responsible for the apparent improvement in the device parameters. Microscopic transport mechanism, however, is not yet clear of the field-induced charge at the crystalline surface. To find out the intrinsic potentials of these organic materials and to foresee further applications of organic devices, extended study of single-crystal OFETs is needed.

Historically, it has been debated for a long time whether poorly doped aromatic organic semiconductors, having the \(\pi\) orbitals of adjacent molecules narrowly overlapped, can realize band transport which justifies the ideal electron-gas picture.6) Regarding the Hall effect, the reported results were controversial even for bulk crystals in terms of sign, temperature dependence and the value, possibly because of difficulty in the measurement of poorly conductive low-temperature dependence and the value, possibly because of difficulty in the measurement of poorly conductive low-

\[R_H \sim \frac{1}{Q}, \text{ where } Q \text{ denotes the charge amount.} \]

Note that the popular expression of Hall coefficient \(R_H \sim 1/Q\), where \(Q\) denotes the charge amount, is realized only when the “charge cloud” is spatially extended to lead to a good conductivity. If the charge is basically localized, on the other hand, \(R_H\) would be much smaller, as is demonstrated for amorphous semiconductors.12,13) In our present study, we use the single-crystal OFETs so that the gate electric field moderately dopes charge in the organic crystalline surface. Detection of sizable Hall effect unambiguously tells us that the charge cloud is well extended.

In our experiments, we crystallized rubrene molecules to a thin platelet with a thickness of approximately 1 \(\mu\)m by physical vapor transport. To fabricate an FET, the thin rubrene crystal is laminated on a SiO\(_2\)/doped Si substrate with gold electrodes patterned for both transverse and longitudinal voltage detections; starting from a SiO\(_2\)/doped Si wafer (SICO, GmbH) with a 500-nm-thick thermally oxidized surface, the SiO\(_2\) surface is spin coated with hexamethildisilane (HMDS) and six gold electrodes were deposited at a thickness of 15 nm by vacuum evaporation through a shadow mask. Figure 1 shows the top view of the device together with an illustration of the measurement configuration. As the transverse signal is only 0.1% of the longitudinal range. The voltage signals are independent of the potential drop at current injecting contacts, so that the potentials \(V_1\) and \(V_2\) at the opposite electrodes are well balanced at zero magnetic field. We trimmed the laminated rubrene crystal into a Hall-bar shape using a scanning laser-etching equipment for this purpose.4) Such a dry-etching process is preferable not to damage the device channel.

Four source measure units (SMUs) equipped in an Agilent Technology E5207 semiconductor parameter analyzer were used for the longitudinal and transverse measurements; one applied the source–drain voltage \(V_D\) applied in the longitudinal direction, it is essential to regulate the current and symmetrically position the two narrow paths from the gold electrodes at both sides so that the potentials \(V_1\) and \(V_2\) at the opposite sides that the potentials \(V_1\) at the opposite electrode are well balanced at zero magnetic field. We trimmed the laminated rubrene crystal into a Hall-bar shape using a scanning laser-etching equipment for this purpose.4) Such a dry-etching process is preferable not to damage the device channel.

Four source measure units (SMUs) equipped in an Agilent Technology E5207 semiconductor parameter analyzer were used for the longitudinal and transverse measurements; one applied the source–drain voltage and measured the drain current \(I_D\), another applied the gate voltage \(V_G\), and the other two detected voltage signals in either transverse or longitudinal directions in the high-impedance voltage-measurement mode. Note that the input impedance of the voltmeter is around \(T\Omega\), which is high enough for our measurement typically in a M\(\Omega\) range. The voltage signals are independent of the potential drop at current injecting contacts, so that purely intrinsic signals from the sample are measured while avoiding contact resistances. Magnetic field was applied perpendicular to the crystalline surface using PPMS (Physical Properties Measurement System, Quantum Design, Inc.). The transverse voltage signals were continuously measured at a sweeping gate voltage from \(-30\) to +30 V in

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15 s and sweeping magnetic field repeatedly in the range of ±10 T with 0.27 T/min.

To detect the Hall effect, the transverse voltage $V_{\text{trans}} (= V_3 - V_1)$ is monitored during the continuous sweep of $V_G$, under a slowly changing magnetic field, $H$, perpendicular to the crystal surface. With repeated sweep of $H$, $V_{\text{trans}}$ gradually changes with time. Plotted in Fig. 2 are the time evolutions of the transverse voltage for several gate voltages, where a slow-drift component of $\sim 10 \text{ mV}$ is already subtracted. The plot apparently shows that $V_{\text{trans}}$ changes concomitantly with the applied magnetic field and has maximum and minimum values at $+10 \text{T}$ and $-10 \text{T}$, respectively, which demonstrates the presence of the Hall effect in OFETs. The Hall coefficient $R_H$ is evaluated as $V_{\text{trans}}/\mu_0 H I_D$, where $\mu_0$ denotes the permeability in vacuum, and inverse $R_H$ is plotted as a function of $V_G$ in the upper panel of Fig. 3. The sign of $R_H$ is positive for all negative $V_G$ (positive $H$ directs as defined in Fig. 1), exhibiting a normal Hall effect of the holes induced by the gate electric field.

For comparison, longitudinal conductance $\sigma$ are measured also as functions of the gate voltage $V_G$. $\sigma$ is evaluated as $I_D/(V_2 - V_1)L/W$ ($L$ and $W$ denote the length and width of the measured portion of the channel), and is plotted together with $I_D$ in Fig. 3. The result well reproduces the standard model of FETs for hole injection, i.e., $\sigma = -C_l(V_3 - V_{th})/\mu_0 L I_D$, where $C_l$ and $V_{th}$ denote the capacitance of the gate insulator and the threshold voltage, respectively. $\mu_{\text{FET}}$ can be evaluated as $\sim 1.5 \text{ cm}^2/(\text{V s})$, which is not as high as the best value $[20 \text{ cm}^2/(\text{V s})]$ reported for the air-gapped single-crystal FET measured in the most conductive direction. Since our thin crystal is placed in the least conductive direction (the a-axis direction) for the measurement, the anisotropy is at least partially responsible for the discrepancy in $\mu_{\text{FET}}$. The transfer characteristics also show considerable positive threshold voltage, indicating additional hole doping at the crystalline surface either by treated SiO$_2$ surface or natural dopants such as oxygen in the bulk crystal.

We detect the Hall voltage only when the crystalline surface has a good conductivity when $V_G < 0$. As does the longitudinal conductivity $\sigma$ plotted together in the upper panel of Fig. 3, $1/R_H$ monotonically increases with $|V_G - V_{th}|$. Moreover, within 30% of the magnitude, $1/R_H$ agrees with $C_l|V_G - V_{th}|$, which is assumed to be the induced surface charge upon the standard model of FETs, as viewed also in Fig. 3. Besides the 30%-discrepancy, the result corresponds to the free-electron model where the charge amount $Q$ is equal to $1/R_H$. The result indicates that a major part of the surface charge is highly mobile so that its electromagnetic character resembles that of extended holes.

To understand the observation in more detail, it is
In our present experiments. It is known that the ratio to the lower panel of Fig. 3, tunnelling (hopping) process in principle. As shown in the provide a transverse electromotive force for a single transport is dominant, because magnetic field does not exceed 0.1 according to theoretical and experimental studies.\(^{12,13}\) In addition, as shown in the inset of Fig. 3, \(\mu_{FET}\) is nearly temperature-independent down to 260 K, which does not resemble \(\mu_{FET}(T)\) profile of hopping transport, either.

The above results indicate consistency in the band transport; however, still the mobility of 1.5 cm\(^2\) V\(^{-1}\) s\(^{-1}\) may be small for an ideal coherent transport for which truly extended wave functions of electrons are responsible. To have an idea of how far the surface holes move, we estimate the mean free path at room temperature \((T = 300\, \text{K})\); the Boltzmann distribution gives average velocity as \(\bar{v} = \sqrt{2k_B T/m^*} \sim 1.1 \times 10^5\, \text{m/s}\) for two-dimensional systems when the effective mass \(m^*\) is nearly equal to that of a free electron. Giving the relaxation time \(\tau = m^*\mu_{FET}/e \sim 10–15\, \text{s}\), where \(e\) denotes the electron charge, the mean free path \(\ell = (\bar{v}\tau \sim 0.11\, \text{nm})\) can be estimated to be half of the lattice constant \(a\), showing apparent difference from typical band metals in which \(\ell \gg a\). Even considering the presence of high-energy particles and assuming mass enhancement by polaronic renormalization,\(^{6}\) \(\ell\) would not be much longer than the lattice constant. Therefore, although the clear observation of a normal Hall effect suggests the extended nature of the surface holes, they appear to be on the verge of localization.

For future studies, the FETs may be a suitable device to investigate how the extended electronic state is achieved when the carriers are doped into the band insulator, as the carrier density is continuously controlled by the gate electric field. The two-dimensional electronic system around the crossover between the extended and localized states is in itself intriguing, analogous to the spontaneous construction of a large-scale network, which is of general interest in the fields of physics, statistics and social science.\(^{15}\) For technologies, further understanding of the character of the holes responsible for the FET action can lead to prescriptions to design higher-performance OFETs, which would pave the way to low-power applications such as logic-circuit components. A device designed to utilize a channel deeper in a crystal, for example, would be useful to provide higher \(\mu_{FET}\) as speculated above. In these aspects, the Hall-effect measurement of OFETs is expected to be a powerful tool in the study of microscopic transport mechanisms, as has been successfully performed for various electronic systems.

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