Wafer-scale, layer-controlled organic single crystals for high-speed circuit operation

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Two-dimensional (2D) layered semiconductors are a novel class of functional materials that are an ideal platform for electronic applications, where the whole electronic states are directly modified by external stimuli adjacent to their electronic channels. Scale-up of the areal coverage while maintaining homogeneous single crystals has been the relevant challenge. We demonstrate that wafer-size single crystals composed of an organic semiconductor bimolecular layer with an excellent mobility of 10 cm² V⁻¹ s⁻¹ can be successfully formed via a simple one-shot solution process. The well-controlled process to achieve organic single crystals composed of minimum molecular units realizes unprecedented low contact resistance and results in high-speed transistor operation of 20 MHz, which is twice as high as the common frequency used in near-field wireless communication. The capability of the solution process for scale-up coverage of high-mobility organic semiconductors opens up the way for novel 2D nanomaterials to realize products with large-scale integrated circuits on film-based devices.

INTRODUCTION

Developments in the synthesis and deposition of large-scale two-dimensional (2D) nanomaterials have motivated researchers to realize an ideal building block for future electronic and optoelectronic devices. The key engineering challenge to the integration of these nanomaterials into high-performance devices and applications is the mass production of large-area films without sacrificing the uniform 2D nature (1, 2). Graphene, group IV elemental sheets (for example, silicene and germanene) (3), and transition metal dichalcogenides (for example, MoS₂, MoSe₂, WS₂, and WSe₂) (4) have been emerging as strong contenders in 2D nanomaterials for electronic and optoelectronic applications. Although the two-dimensionality offers unique and excellent electronic properties, the ideal production of uniform, large-area monolayer (1L) sheets with reasonably high efficiency and yield has yet to be realized (2). Unlike nanosheets composed of an atomic layer, organic semiconductors (OSCs) form quasi-2D single crystals, where molecules are weakly bonded by van der Waals interaction instead of covalent bonds. This not only offers potential for chemical design but also room temperature solution processing.

Recent intensive studies on the development of OSC compounds have been highlighted by an improvement of the carrier mobility up to 10 cm² V⁻¹ s⁻¹ (3–8), which constitutes one step forward toward printable, wearable device applications. Most of these applications, such as radio-frequency identification (RF-ID) tags (9, 10) and large-scale integrated circuits that drive multiple sensors (11–13), will require relatively high-speed circuit operation and large-area coverage. Many researchers have attempted to realize layer-controlled, wafer-scale organic single-crystalline semiconductors. For example, organic field-effect transistors (OFETs) using few-layered organic single crystals as an active semiconductor layer have been reported for several materials (14–17). Few-layer single crystals of pentacene and diocetylbenzothienobenzothiophene grown epitaxially on atomically flat 2D boron nitride substrates exhibit high mobility (14, 15). However, these ultrathin crystals, which are normally composed of only a few molecular units (approximately 10 nm), can be fabricated only on a particular substrate with lattice constant matching; thus, their application is considerably limited. Although it has been reported that ultrathin single-crystalline films can also be grown via various solution-coating processes, such as drop casting (17), dip coating (18), and an air flow–driven assembly technique (13), there are some difficulties with respect to the crystal uniformity and/or coverage of the resultant films. Among these techniques, a meniscus-driven solution-processed method can promise scaling-up of uniform organic crystals (19–22), although state-of-the-art organic single-crystalline films have yet to be demonstrated.

Here, we successfully demonstrate the selective deposition of 1L, bilayer (2L), and trilayer (3L) molecular single crystals with wafer-scale coverage by optimization of the meniscus-driven crystal growth technique. 2L-OFETs show the best performance with a mobility that reaches up to 13 cm² V⁻¹ s⁻¹, and the channel width–normalized contact resistance extracted by the transmission line method (TLM) is 46.9 ohm-cm, which is, to the best of our knowledge, the lowest value reported for OFETs. In addition, high-frequency operation of the 2L-OFET is confirmed with a channel length of 3 μm. The high mobility and minimized contact resistance of the fabricated 2L-OFET resulted in a cutoff frequency of 20 MHz, and a diode-connected 2L-OFET functioned as a high-speed rectifier that can convert ac signals to dc voltages at frequencies up to 29 MHz.

RESULTS AND DISCUSSION

Fabrication and characterization of ultrathin organic single crystals

Unlike conventional 2D materials, the present organic single-crystalline thin films can be deposited directly onto any given substrate via a
simple one-shot solution process. A single crystal of one of our benchmarked materials, 3,11-dioctylindinaphtho[2,3-d:2′,3′-d′]benzo[1,2-b:4,5-b′]dithiophene (C8-DNBDT-NW), which is synthesized and purified in-house (fig. S1), was formed via the meniscus-driven solution method (that is, continuous edge casting; Fig. 1A). The decent solubility of C8-DNBDT-NW contributes to lower the process temperature down to 60° to 70°C (see table S1 and fig. S2 in section S1), which provides ideal fabrication conditions for ultrathin single crystals composed of a few molecular layers. In the present crystal growth technique, solvent evaporation occurs at the edge of the meniscus region of a droplet retained at a shearing blade, which promotes crystallization from a supersaturated zone of the solution. The solute precipitation rate is critically influenced by the amount of solvent evaporation; therefore, the process temperature, shearing rate of the substrate, and the solution concentration (see details in section S2) are adjusted to control the number of layers from 1L to multilayer while achieving large-area coverage. The formation of single-crystalline films was confirmed by cross-polarized optical microscopy observations (Fig. 1, B and C). When the crystal growth direction is parallel or perpendicular to the polarization angle, a completely black image is obtained, which indicates that the crystal axes are highly oriented. The film thickness estimated from atomic force microscopy (AFM) observations was determined to be approximately 7.2 nm, which is equivalent to the height of two molecular layers (Fig. 1D). The single-crystalline domain continues over a few centimeters, which is sufficiently long to cover several hundreds of transistors as confirmed by the scanning electron microscopy (SEM) image shown in Fig. 1E, where brighter and darker regions are 1L and 2L domains, respectively (figs. S13 and S14). The thickness of the single crystal is easily evaluated by the different color contrasts in the polarized optical microscopic images (Fig. 2, A to C). In addition, excellent scalability of the thickness was confirmed by Raman spectroscopy measurements. Figure 2D shows Raman spectra taken for 1L, 2L, and 3L single crystals, where the peak assigned to an intramolecular vibration increases linearly with respect to the number of layers (figs. S15 and S16).

**OFET performance of ultrathin single crystals**

To evaluate electric properties, OFETs were fabricated with 1L, 2L, and 3L single crystals by subsequent deposition of 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) (23) and gold through a shadow mask. Figure 2E shows the two-terminal conductivity $\sigma_{TE}$ for the 1L-, 2L-, and 3L-OFETs. The 2L- and 3L-OFETs exhibit textbook-like performance with a near-zero threshold voltage and mobility of more than 10 cm$^2$ V$^{-1}$ s$^{-1}$, whereas the mobility of the 1L-OFET was two orders of magnitude lower (figs. S5 to S8). To address this reduction in mobility for the 1L film, the crystal packing structures in 1L and 2L single crystals were investigated using transmission electron microscopy (TEM). Figure 2 (F to I) shows TEM images and selected-area electron diffraction (SAED) patterns of the rectangular unit cells for the 1L and 2L single crystals, which are assigned to a herringbone packing structure in the bulk of the C8-DNBDT-NW crystal (figs. S3 and S4). This indicates that the microscopic crystal structures of the 1L and 2L single crystals are essentially identical. Note that either a broader diffraction spot or a doubly overlapped peak is often found in the SAED patterns of 1L single crystals (figs. S17 to S19), which implies that there is a finite fraction of unavoidable defects and lattice mismatches in 1L single crystals.

We consider that these imperfections of the first layer give rise to the significant decrease in mobility. In addition, the lack of disorder patterns in the 2L crystals can be explained as a sufficient amount of organic molecules being supplied during formation of the 2L crystal, which is likely to relax the defects in the first layer.

**Contact resistance evaluation**

We now turn the discussion to the contact resistance effect. In most OFETs, carrier injection and extraction at the source and drain electrodes occur at a heterojunction between the OSC and metal electrodes. The interfacial contact resistance often dominates the transistor characteristics, so that high-frequency operation is likely to be limited. Both the interfacial and access resistance of the bulk OSC contributes to the net contact resistance in a top-contact, bottom-gate geometry, because charge carriers should travel along the relatively resistive out-of-plane direction of the organic layer from the electrode to the channel. A reduction of the organic layer thickness can significantly reduce the net contact resistance. To address the influence of contact resistance, the gated four-point probe (gFPp) method was used to evaluate the 2L- and 3L-OFETs (fig. S9). Figure 2J shows the four-terminal sheet conductivity $\sigma_{s}$ as a function of gate voltage, $V_G$. No apparent difference of $\sigma_{s}$ for the 2L and 3L films was observed, and the mobilities of both reached up to 13 cm$^2$ V$^{-1}$ s$^{-1}$. This suggests that the present 2L film is sufficiently thick for ideal carrier transport. To further investigate the contact resistance, the gFPp method was adapted to examine the output characteristics. The voltage drop at the source electrodes $\Delta V_{cs}$, shown in the horizontal axis, is extracted from the effective channel potential (see details in section S2). In the 2L-OFET, the drain current, $I_D$, is almost perfectly proportional to $\Delta V_{cs}$ over broader $\Delta V_{cs}$ ranges, which means that ohmic contact is established (Fig. 2K). On the other hand, a superlinear dependence in $I_D$-$\Delta V_{cs}$ is obtained for the 3L-OFET,
and the superlinearity is more apparent in the lower $\Delta V_{cs}$ region (Fig. 2J), which indicates that the excess layer is likely to behave as a Schottky barrier. To qualitatively analyze the contact resistance, $R_C$, several transistors were fabricated with different channel lengths for 2L and 3L single-crystalline films, and their contact resistance was extracted by the TLM (Fig. 3A and figs. S10 to S12). Figure 3 (B and C) shows the width-normalized total resistance ($R_{C-W}$) as a function of the gate voltage ($V_G$). The large single-crystalline film has a length of more than a few centimeters, so that the contact resistance can be extrapolated with high accuracy, which is confirmed by a high square of the regression coefficient ($R^2$) of 0.99 over the total $V_G$. A comparison of $R_{C-W}$ for the 2L- and 3L-OFETs with various $V_G$ reveals $R_{C-W}$ for the 2L-OFET to be less than that obtained for the 3L device by a factor of 5, as shown in Fig. 3D. This result supports the idea that the contact resistance of top-contact OFETs can be controlled and significantly reduced by a decrease in the film thickness. $R_{C-W}$ for the 2L-OFETs is $V_G$ invariant, whereas the contact resistance has $V_G$ dependence for typical top-contact OFETs, which is often considered to be caused by the trap states in the access region (24–26). The observed $V_G$ invariant contact resistance can be explained by the presence of an F$_4$-TCNQ layer inserted between the organic layer and the metal electrode. The additional molecular dopant layer is often used to improve charge injection because the dopant layer effectively reduces the trap states. The access region in 2L films is equivalent only to the secondary layer, which is directly attached to acceptor F$_4$-TCNQ molecules; therefore, the interfacial doping becomes more effective compared to 3L single-crystalline films. Thus, it was concluded that F$_4$-TCNQ can fill the trap density of states in the access region of 2L films, which results in $V_G$-independent contact resistance. This is consistent with the $I_D-\Delta V_{cs}$ characteristics (shown in Fig. 2, K and L). The interface between Au- and F$_4$-TCNQ-doped OSC layers for 2L-OFETs is realized in an ideal ohmic contact, whereas the excess, undoped OSC layer for 3L-OFETs can be the space-
charge layer, resulting in the superlinear $I_D$-$\Delta V_{ds}$ characteristics. We do not speculate on the mechanism of doping but merely note that understanding charge transport/injection mechanism at the metal/organic interface will be a key issue to further reduce the contact resistance (27). $R_C$-$W$ for 2L-OFETs is determined to be 46.9 ohm-cm at a gate voltage of $-30$ V, which is, to the best of our knowledge, the lowest contact resistance reported for any OFETs except for electrolyte-gated transistors with the contact strongly doped by ionic gel (28). In electrolyte-gated transistors, ions penetrate from the dielectric gel into the semiconductor, which results in extremely low contact resistance. However, this electrochemical doping occurs only at low switching frequencies of less than 1 kHz (29). For the purpose of transistor application to high-frequency devices, 2L-OFETs, with the adoption of a special doping mechanism, are more favorable in terms of the operation speed.

**High-frequency measurement**

Both high mobility and very low contact resistance in 2L single-crystalline films allows for an ideal device that will enable high-speed operation. To evaluate the dynamic response, a 2L-OFET with a channel length of a few micrometers was fabricated. Figure 4A shows a schematic image of the short-channel transistor for high-frequency measurements, which includes patterned gate, source, and drain electrodes fabricated via multiple photolithographic processes (30). The channel length ($L$) and the total overlap length between the gate and the source/drain electrodes ($L_C$) were measured to be approximately 3 and 4.5 μm, respectively (Fig. 4B). The transfer and output properties are shown in Fig. 4 (C and D, respectively), where a reasonably high on/off ratio of more than $10^3$ is achieved, even with the relatively short channel length. Thus, no apparent short channel effect is observed. The effective mobility ($\mu_{\text{eff}}$) extracted from the slope of the transfer curve is estimated to be 2.7 cm$^2$ V$^{-1}$ s$^{-1}$ (Fig. S20), which is much lower than the intrinsic mobility ($\mu_{\text{int}}$) obtained from the gFPP measurement. The empirical relation between effective and intrinsic mobility is expressed as (31)

$$\mu_{\text{eff}} = \frac{\mu_{\text{int}}}{1 + \frac{R_C}{L} \mu_{\text{int}} G_C (V_G - V_{\text{th}})}$$

where $G_C$ is the gate capacitance per unit area of the gate insulator and $V_{\text{th}}$ is the threshold voltage. Note that although 2L single crystals exhibit ultralow contact resistance, the influence of contact resistance is still dominant in a short-channel device with a channel length of a few micrometers, which results in a significant reduction of the effective mobility.

The cutoff frequency ($f_T$), which is the maximum operational frequency of an individual transistor, is described by the following equation

$$f_T = \frac{\mu_{\text{eff}} V_D}{2 \pi L (L + L_C)}$$

where $V_D$ is the applied drain voltage. $f_T$ is defined as the frequency at which the current gain is zero, which means the gate current is equal to the drain current. Figure 4E shows a schematic diagram of the setup for the cutoff frequency measurement (32). Both the gate and drain dc voltages were set to $-10$ V.

The cutoff frequency is extracted to be 20 MHz from the frequency when the amplitude of the gate current ($\Delta I_G$) is the same as that of the drain current ($\Delta I_D$), as shown in fig. S21, which is in agreement with the theoretically calculated value of 19 MHz based on Eq. 2. The obtained cutoff frequency is compared with several previous works summarized in table S4. Note that because $f_T$ is proportional to the drain voltage, the $V_D$-normalized cutoff frequency is an index for comparison. The cutoff frequency obtained in this study is the highest value for solution-processed devices to our knowledge. In addition, the present 2L-OFET has a slightly longer channel length than that in previous work; therefore, by further reducing the channel length, there should be more room for the improvement of the operational speed.

A high-speed organic rectifier plays a paramount role in achieving low-cost RF-ID tags based on OSCs because the rectifier supplies a dc voltage to the entire circuit on the tags. There are two different approaches to the fabrication of organic rectifiers: a vertical organic diode, where a semiconducting layer is sandwiched between two metal electrodes with different work functions, and, alternatively, a diode-connected OFET. The former approach has a significant geometrical advantage to obtain high-speed response; the effective channel approximates the thickness of the organic layers (33, 34). However, this configuration is vulnerable to a large voltage produced by electromagnetic induction and to Joule heating (35). Therefore, a diode-connected OFET with sufficient insulating capability is more suitable for wireless communication with RF-ID tags. The rectification characteristics of the diode-connected 2L-OFET were measured using the circuit shown in Fig. 5A. The charges passing through the diode are accumulated in the capacitor to produce an output dc voltage ($V_{\text{out}}$). Figure 5 (B and C) shows the
rectifying characteristics at 1 and 25 MHz, where an ac voltage (V_in) with an amplitude of 8 V is applied. The result indicates that the input ac signal can be converted into a constant dc voltage. Figure 5C shows the frequency dependence of the V_out. When the maximum rectifying frequency (f_rectify) is defined as the frequency at which V_out is decreased by a factor of −3 dB, f_rectify is extracted to be 29 MHz from Fig. 5D. f_rectify is expressed as (36)

$$f_{\text{rectify}} = \frac{\mu_{\text{eff}} V_0}{2L^2} \left( \sqrt{1 - \frac{\beta^2}{\cos^2 \beta}} - \beta \right)$$

where $V_0$ is the amplitude of the input ac voltage and $\beta$ represents $V_{\text{out}}/V_0$. The theoretical $f_{\text{rectify}}$ calculated from Eq. 3 is 37 MHz, which is larger than the experimental value. This discrepancy may be due to the voltage dependence of $\mu_{\text{eff}}$. Equation 3 assumes that $\mu_{\text{eff}}$ is a constant parameter; therefore, the mobility is fixed to 2.1 cm² V⁻¹ s⁻¹ as the maximum operated value at $V_G = -4.7$ V (see more details in fig. S20). Because $\mu_{\text{eff}}$ is reduced under the influence of its gate dependence, $\mu_{\text{eff}}$ that is averaged over the low-voltage regime is diminished to 1.8 cm² V⁻¹ s⁻¹ (see more details in section S4 and fig. S20), resulting in a theoretical $f_{\text{rectify}}$ value of approximately 31 MHz, which is in agreement with experiments. The $f_{\text{rectify}}$ of 29 MHz is more than twice as high as the commonly used frequency in near-field communication of RF-ID tags (13.56 MHz), although the applied voltage is half of that in our previous report (36).

In conclusion, we have successfully demonstrated a wafer-scale, layer-controlled organic single-crystalline film composed of only a few molecular layers and achieved a sufficiently high carrier mobility of 13 cm² V⁻¹ s⁻¹ together with an extremely low contact resistance of 46.9 ohm·cm. Optimization of the meniscus-driven solution crystallization technique developed in-house is expected to scale up the areal coverage of the layer-controlled ultrathin single-crystalline films. The present one-shot deposition method is applicable to any given substrate. These state-of-the-art 2D molecular crystal sheets allow high-frequency operation with a channel length of 3 μm and response at a frequency of 20 MHz with an applied voltage of −10 V. Furthermore, a diode-connected 2L-OFET exhibits a rectifying capability of up to 29 MHz, which is higher than the commonly used frequency in the wireless communication of RF-ID tags. We consider this technique for the fabrication of ultrathin single crystals to contribute to the realization of high-speed organic electronic devices. The two-dimensional molecular crystal sheets demonstrated here could serve as useful scaffolds not only for the integration of functional materials into high-performance devices but also for the realization of groundbreaking functionalities in OSCs.

**MATERIALS AND METHODS**

**Fabrication of devices for contact resistance evaluation**

A 100-nm-thick Si substrate with a thermally grown SiO₂ layer was cleaned with acetone and 2-propanol and then treated by an ultraviolet-ozone process. A self-assembled monolayer (SAM) of 2-(phenylhexyl)trimethoxysilane was deposited on the surface by vapor deposition at
120°C for 3 hours. Organic crystalline films of C$_8$-DNBDT-NW were then grown from a 0.02–weight % chlorothiophene solution using the continuous edge-casting technique described in our previous work (21, 37). The substrate was heated up to 60° to 70°C and moved with a shearing rate of 20 μm s$^{-1}$ while a blade was fixed 100 μm above the substrate. The thickness of the crystalline films was mainly controlled by changing the substrate temperature; 1L, 2L, and 3L single crystals were obtained with substrate temperatures of 58° to 60°C, 60° to 62°C, and 65°C, respectively. After annealing the substrate at 80°C in vacuum to remove residual solvent, F$_2$-TCNQ and Au were subsequently deposited through a metal mask to form source/drain electrodes. Organic layers were patterned by dry-etching processes with an yttrium-aluminum-garnet laser (266 nm).

**Fabrication of short-channel devices**

Thermally evaporated Ag layers were patterned by conventional photolithography to form gate electrodes. A 100-nm-thick aluminum oxide layer was deposited by an atomic layer deposition technique as a gate dielectric layer. The surface of the aluminum oxide was then treated with a 2-(phenylhexyl)phosphonic acid SAM by immersing the substrate into a 0.2 mM solution for 13 hours. Organic layers were fabricated by almost the same process conditions as those for crystal growth. Source and drain electrodes were patterned by multiple lithographic processes, where OSCoR4001 (Orthogonal Inc.) and AURUM S-50790 (Kanto Chemical Co. Inc.) were used as a photoresist and a gold etchant, respectively.

**Electrical measurements**

All measurements were performed under ambient conditions. The transistor properties were measured using a semiconductor parameter analyzer (Keithley 4200-SCS). Dynamic measurements to evaluate the cutoff frequency were conducted using the same setup as that reported previously (32). ac signals with a peak-to-peak voltage of 1 V [$v_g(t)$] were generated using a function generator (Tektronix AFG3102), and dc gate (V$_G$) and drain (V$_D$) voltages of –10 V were generated using the same semiconductor parameter analyzer. The synthesis voltage [$v_g(t)$] + V$_G$ was applied to the gate electrode using a bias tee (ZFBT–4R2GW+, Mini Circuits). The output gate and drain currents were measured using an oscilloscope (Tektronix MDO3041) with current probes (Tektronix CT-6). Measurement of the rectifying characteristics was performed using another function generator (Tabor Electronics WS8102) to apply an input voltage, and an oscilloscope (Teledyne LeCroy HDO4054) was used to read the input and output current signals.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/4/eaao5758/DC1 section S1. Materials section S2. Details of transport measurements section S3. Characterization of single crystals section S4. Details of high-frequency measurements fig. S1. Scheme for the synthesis of C$_8$-DNBDT-NW. fig. S2. Phase transition temperature and melting point of C$_8$-DNBDT-NW. fig. S3. Structure, transfer integrals, and effective masses of C$_8$-DNBDT. fig. S4. Crystal packing structure of C$_8$-DNBDT-NW. fig. S5. Effect of thermal annealing on the transfer characteristics of 2L C$_8$-DNBDT-NW FET. fig. S6. Device characteristics of 1L C$_8$-DNBDT-NW FET. fig. S7. Device characteristics of 2L C$_8$-DNBDT-NW FET. fig. S8. Device characteristics of 3L C$_8$-DNBDT-NW FET. fig. S9. Estimation of contact resistance by the gFPP method.

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