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# High mobility field-effect transistors produced by direct growth of C<sub>70</sub> single crystals from a solution†

Yuto Sakai,<sup>a</sup> Taiyo Araki,<sup>a</sup> Ryo Suzuki,<sup>id</sup><sup>a</sup> Toshiyuki Sasaki,<sup>id</sup><sup>b</sup> Kouhei Ichianagi,<sup>b</sup> Tadahiko Hirai,<sup>id</sup><sup>c</sup> Nobuyuki Aoki<sup>d</sup> and Masaru Tachibana<sup>id</sup><sup>\*a</sup>

Fullerene C<sub>70</sub> crystals are n-type semiconductor materials that are used in organic field-effect transistors (OFETs). However, research on C<sub>70</sub> FETs has so far been limited to low electron mobilities below  $\sim 10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. To achieve higher mobilities, it is essential to enhance the electrical contact between C<sub>70</sub> crystals and the FET substrate with electrodes, as well as to grow high-quality crystals. In this study, high-mobility FETs were produced by directly growing C<sub>70</sub> crystals from a C<sub>70</sub> saturated *m*-xylene solution. Good electrical contact between the C<sub>70</sub> crystals and FET substrates with electrodes is realized in a bottom-gated bottom-contact FET configuration. The resulting rhombohedral shaped C<sub>70</sub> crystals exhibited solvated hexagonal structures with lattice parameters of  $a = 50.52$  Å and  $c = 24.70$  Å. These directly grown C<sub>70</sub> crystal FETs exhibited typical n-type output and transfer characteristics. The electron mobility improved after annealing at 100 °C in a vacuum, which is probably due to the desorption of H<sub>2</sub>O and O<sub>2</sub> in the crystals, although the solvation in the crystals was preserved. The solvated C<sub>70</sub> crystal FETs achieved a high electron mobility of 1.14 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> which is an improvement of more than two orders of magnitude relative to previously documented C<sub>70</sub> FETs, demonstrating the potential of C<sub>70</sub> crystals for use in electronic devices.

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## Introduction

Fullerene C<sub>60</sub> and C<sub>70</sub> crystals are n-type semiconductor materials.<sup>1,2</sup> Among them, C<sub>60</sub> crystals have been extensively studied for use in organic field-effect transistors (OFETs). The electron mobility of C<sub>60</sub>-based FETs is 0.08–3.23 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in thin-film devices<sup>1,3–6</sup> and 0.002–0.0382 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in single-crystal devices.<sup>7–11</sup> These FETs are typically fabricated in a bottom-contact configuration. In contrast, top-contact configurations have achieved higher mobilities of over 1 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in both FETs based on thin films<sup>5,12,13</sup> and C<sub>60</sub> single-crystal needles aligned by controlled growth.<sup>14–17</sup> The highest reported electron mobility is 11 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>,<sup>14</sup> placing C<sub>60</sub> among the most promising n-type semiconductors.<sup>18</sup>

C<sub>70</sub> has a similar electronic state to C<sub>60</sub>, although the lowest unoccupied molecular orbital (LUMO) energy level of C<sub>70</sub> is slightly lower than that of C<sub>60</sub>.<sup>10,11,19–21</sup> The lower LUMO level of C<sub>70</sub> compared to that of C<sub>60</sub> may reduce the energy barrier for electron injection from electrodes, when gold is used as an electrode in FETs, as previously reported. Therefore, C<sub>70</sub> is expected to exhibit superior FET performance, similar to that of C<sub>60</sub>. However, studies on OFETs based on C<sub>70</sub> are limited to thin films with low crystallinity, owing to the difficulty in growing high-quality single crystals. Moreover, the electron mobility in thin C<sub>70</sub> films is 0.002–0.066 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>,<sup>2,4</sup> which is relatively low compared to that of C<sub>60</sub>.

Studies on C<sub>70</sub> FETs using single crystals with a bottom-contact configuration have also been conducted. However, the measured value for electron mobility was  $\sim 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>,<sup>20–22</sup> which is lower than that of the aforementioned thin C<sub>70</sub> films. Even C<sub>70</sub> FETs using needle-like single crystals have a maximum electron mobility of only  $1.32 \times 10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>,<sup>23</sup> which is comparable to that of thin films. As for the output characteristics of the C<sub>70</sub> needle crystal FETs, the drain current slowly increased with the drain voltage in the low-voltage region. Moreover, no clear saturation of the drain current was observed, even at higher voltages. This behavior can be attributed to the poor or non-ohmic contact between the C<sub>70</sub> crystal and the FET substrate with the electrodes. In these devices, C<sub>70</sub> needle

<sup>a</sup> Department of Materials System Science, Yokohama City University, 22-2 Seto, Kanazawa-ku, Yokohama 236-0027, Japan. E-mail: tachiban@yokohama-cu.ac.jp<sup>b</sup> Japan Synchrotron Radiation Research Institute, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan<sup>c</sup> CSIRO Manufacturing, Research Way Clayton, Victoria 3168, Australia<sup>d</sup> Department of Materials Science, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d5tc01627d>

crystals grown in solution were simply dropped and dried onto the FET substrate to bridge the source and drain electrodes.

To achieve enhanced FET characteristics and higher electron mobility, the electrical contact between the C<sub>70</sub> crystals and the FET substrates with the electrodes has to be improved. The top-contact configuration in FET devices is useful to improve the electrical contact. However, fabrication of the top-contact configuration is difficult owing to the small size of the C<sub>70</sub> crystals. In addition, the C<sub>70</sub> crystals can be damaged at high temperatures when metal electrodes are thermally deposited on the crystals in the top-contact configuration. In this paper, a high-mobility FET fabricated by direct growth of C<sub>70</sub> crystals from a solution for improved electrical contact in a bottom-contact configuration is reported.

Solution processing techniques such as drop casting, solution shearing, dip coating, spin coating and printing techniques have previously been used successfully for the fabrication of high-mobility organic crystal FETs.<sup>24,25</sup> In this work, a simple solution evaporation method was applied for the fabrication of C<sub>70</sub> single crystal FETs for the first time. The solvated C<sub>70</sub> crystal FETs exhibited electron mobility that was more than two orders of magnitude higher than that reported for previous C<sub>70</sub> FETs, highlighting the potential of C<sub>70</sub> crystals for electronic applications.

## Experimental

### Crystallization and characterization

A solution evaporation method was used for direct crystal growth on the FET substrate. The solution used was *m*-xylene saturated with C<sub>70</sub> (C<sub>70</sub>-*m*-xylene). To optimize the crystallization conditions, crystals were grown under various conditions, such as varying amounts and temperature of the solution and evaporation time. C<sub>70</sub> crystals with rhombohedral shapes and clear crystal behavior are commonly obtained under various conditions, although the size and number of crystals obtained depend on the growth conditions. Fig. S1 (ESI<sup>†</sup>) shows C<sub>70</sub> crystals with rhombohedral shapes grown on the SiO<sub>2</sub>-Si substrate. This study focused on C<sub>70</sub> crystals with rhombohedral shapes as they are more stable compared to other needle crystals.

The morphology and size of the solution-grown C<sub>70</sub> crystals were observed by optical microscopy (BX51, OLYMPUS) and scanning electron microscopy (SEM, S-4300, HITACHI). The crystal structure of the C<sub>70</sub> crystals with rhombohedral shapes was determined by powder X-ray diffraction (PXRD) with Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) (D8-ADVANCE, BRUKER) and single crystal X-ray diffraction (SCXRD) at SPring-8 (BL40XU) with synchrotron radiation ( $\lambda = 0.81 \text{ \AA}$ ). For SCXRD, the crystal data were collected at 100 K with a detector distance of 50.5 mm, a chi value of 45°, a 2 $\theta$  value of 25°, an omega range from -90° to 90°, a delta omega value of 0.2°, and phi values of 0°, 90°, 180°, and 270°. Data integration was performed using CrysAlisPro software (Rigaku OD, 2024). The chemical composition was confirmed by Fourier-transform infrared spectroscopy (FT-IR, FT/IR-410, JASCO) with an attenuated total reflection prism

(ATR PRO ONE, JASCO). It was also confirmed by thermogravimetric (TG) analysis (STA7300, HITACHI) at a heating rate of 10 °C min<sup>-1</sup> in air, where the heating temperature was 25 to 600 °C.

### FET device fabrication

FETs with rhombohedral shaped C<sub>70</sub> crystals were constructed in a bottom-gated bottom-contact configuration. An n<sup>++</sup>-Si wafer with a thermally grown SiO<sub>2</sub> insulating layer (300 nm) was used as the substrate. Interdigital array electrodes of the Au/Cr (40/10 nm) source and drain were fabricated by photolithography on the surface of SiO<sub>2</sub>. An FET substrate with electrodes was used to fabricate the C<sub>70</sub> crystal FETs.

A schematic representation of the FET substrate with the electrodes is shown in Fig. S2 in the ESI.<sup>†</sup>

C<sub>70</sub> crystals with rhombohedral shapes were grown directly on FET substrates with electrodes. The FET fabrication procedure is shown schematically in Fig. S3 (see the ESI<sup>†</sup>). First, the FET substrate was sequentially washed with acetone, IPA, and distilled water for 2 min each. If dirt remained, washing was repeated with IPA and distilled water. The FET substrate was further irradiated with a UV lamp (UV253MINI R, Filgen) for 25 min to remove impurities.

The cleaned FET substrate was placed in a Petri dish (diameter: 3 cm). Subsequently, 0.7 mL C<sub>70</sub> *m*-xylene solution was injected into the Petri dish. The Petri dish was then partially covered with a plate and kept for 30 min at 20 °C. By partially covering the Petri dish, the evaporation of the solvent can be controlled so that the number of nucleation sites for crystallization can be suppressed.

The crystallized FET substrate was then removed from the Petri dish and allowed to dry naturally in air. Consequently, some C<sub>70</sub> crystals with rhombohedral shapes were then grown directly on the FET substrate. Crystallization occurs preferentially at the step edges of the electrodes on the FET substrate, as shown in Fig. S4 (ESI<sup>†</sup>). Thus, some C<sub>70</sub> crystals with rhombohedral shapes could be successfully grown between the electrodes. The electrical properties of the obtained FETs with the rhombohedral C<sub>70</sub> crystals were measured.

### Current-voltage measurements

Current-voltage measurements were performed under 3.0–4.0 × 10<sup>-3</sup> Pa in the dark using a semiconductor parameter analyzer (B1500A, KEYSIGHT). To remove the adsorbed H<sub>2</sub>O and O<sub>2</sub>, the fabricated device was annealed at 100 °C under 3.0–4.0 × 10<sup>-3</sup> Pa for approximately 25 days. The FET characteristics were evaluated without exposing the devices to the ambient atmosphere.

The electron mobility was calculated as follows:

$$\mu = \frac{2L}{WC} \left( \frac{\partial \sqrt{I_{DS}}}{\partial V_G} \right)^2,$$

where  $\mu$  is the electron mobility,  $L$  is the average length of the contact region with the insulating layer,  $W$  is the total width of the crystals on the FET substrate,  $C$  is the electrical capacity of



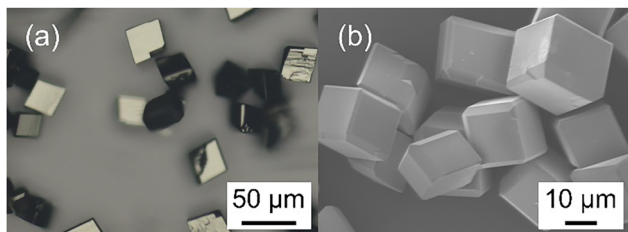


Fig. 1 (a) Optical micrograph and (b) SEM image of rhombohedral shaped  $C_{70}$  crystals grown from a  $C_{70}$ -*m*-xylene solution.

the insulating layer,  $I_{DS}$  is the source–drain current, and  $V_G$  is the gate voltage.  $W$  and  $L$  were measured using scanning electron microscopy (SEM), as shown in Fig. 1.  $W$  is defined as

$$W = \frac{W_1 + W_2}{2}$$

## Results and discussion

### Solution-grown $C_{70}$ crystals

To determine the structure and composition of  $C_{70}$  crystals with rhombohedral shapes, many crystals were grown using the solvent evaporation method. The crystals obtained had rhombohedral shapes with clear crystal habits (Fig. 1), although the size and number of crystals depended on the amount and temperature of the solution and the evaporation time. Fig. S5 (ESI<sup>†</sup>) shows optical micrographs of  $C_{70}$  crystals from different saturated solutions prepared at 5 °C, 20 °C and 40 °C, respectively.  $C_{70}$  crystals with two types of shapes such as rhombohedral and needle shapes were obtained. The ratio of the two shapes depends on the saturated solution. The ratio of

rhombohedral crystals was predominant using the saturated solution prepared at a lower temperature of 5 °C, while needle crystals were predominant using the saturated solution prepared at a higher temperature of 40 °C. The rhombohedral crystals which are stable and of high quality were used in this work. Regardless of the size and number of rhombohedral crystals, they had the same crystal structure and chemical composition.

The chemical composition of the solution-grown  $C_{70}$  crystals with rhombohedral shapes was confirmed by FT-IR spectroscopy. Fig. 2(a) shows the FT-IR spectra around 600–1500  $\text{cm}^{-1}$  for the solution-grown crystals after drying in air for one day and after annealing at 100 °C under  $3.0\text{--}4.0 \times 10^{-3}$  Pa for 11 days. The FT-IR spectra of *m*-xylene used as the solvent and the sublimation-grown  $C_{70}$  crystals including no solvent are also shown in the figure. Many peaks in the solution-grown  $C_{70}$  crystals are observed in the sublimation-grown  $C_{70}$  crystals, which are associated with the vibrational modes of the  $C_{70}$  molecules.<sup>26,27</sup> In contrast, some peaks indicated by filled triangles in Fig. 2(a) are not observed in the sublimation-grown  $C_{70}$  crystals but correspond to those in *m*-xylene. These peaks are associated with the vibrational modes of *m*-xylene. The solution-grown  $C_{70}$  crystals thus comprise  $C_{70}$  and *m*-xylene, which suggests a solvated structure.

The FT-IR peaks of the solution-grown crystals were shifted by 2–4  $\text{cm}^{-1}$  compared to those of the sublimation-grown crystals and *m*-xylene. The slight shift reflects the intermolecular interaction between the  $C_{70}$  molecules and the *m*-xylene molecules, as previously reported for  $C_{60}$  solvated crystals.<sup>28</sup> In addition, the FT-IR peaks in the solution-grown crystals composed of  $C_{70}$  and *m*-xylene remained almost unchanged even after annealing at 100 °C in a vacuum. This indicates that

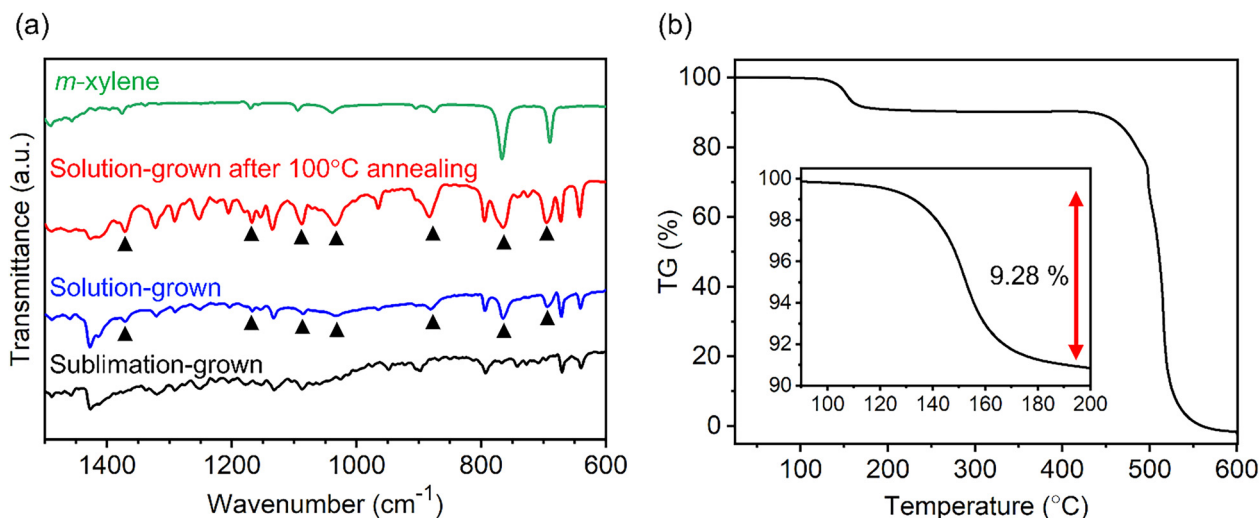


Fig. 2 (a) Blue and red lines show the FT-IR spectra after drying  $C_{70}$  crystals with rhombohedral shapes grown from a  $C_{70}$ -*m*-xylene solution in air for one day and after annealing them at 100 °C for 11 days under  $3.0\text{--}4.0 \times 10^{-3}$  Pa, respectively. For reference, the FT-IR spectra of sublimation-grown  $C_{70}$  crystals without a solvent and *m*-xylene as the solvent are also shown in the figure. The peaks corresponding to those of *m*-xylene are indicated by filled triangles. (b) TG curve of  $C_{70}$  crystals with rhombohedral shapes grown from  $C_{70}$ -*m*-xylene solution. The inset shows an enlarged view in the temperature range from 90 °C to 200 °C. The TG curve was recorded at a heating rate of 10 °C  $\text{min}^{-1}$  in air.



the solvated structures of C<sub>70</sub> and *m*-xylene were preserved under the annealing conditions used in this study.

TG measurements were performed to better understand the chemical composition of the solution-grown C<sub>70</sub> crystals with rhombohedral shapes. Fig. 2(b) shows the TG curves of the solvated C<sub>70</sub> crystals in air. Weight losses were observed at 140–165 °C and 491–532 °C, which can be related to the desorption of *m*-xylene and sublimation of C<sub>70</sub> molecules, in the solvated C<sub>70</sub> crystals, respectively. The desorption temperature of 140–165 °C of *m*-xylene is consistent with the fact that the *m*-xylene-solvated structure is retained even upon annealing at 100 °C as is evident in the FT-IR spectra of Fig. 2(a).

The weight loss corresponding to the desorption of *m*-xylene was approximately 9.28% (Fig. 2(b)). Assuming the aforementioned weight loss and molecular weights of 840.77 and 106.17 of C<sub>70</sub> and *m*-xylene, respectively, the composition ratio of C<sub>70</sub> and *m*-xylene in the solvated C<sub>70</sub> crystals with rhombohedral shapes is estimated to be approximately 10 : 8. The composition ratio was similar to that of solvated C<sub>70</sub> needle crystals grown by the liquid–liquid interfacial precipitation method with two types of solvents, *m*-xylene and IPA, as reported previously.<sup>23,29</sup> This indicates that the crystal morphology changes considerably depending on the growth method, even if the crystals have almost the same solvent composition ratio. The slight discrepancy in the solvation ratio could be related to crystal morphologies, such as needle and rhombohedral shapes.

The XRD patterns of the solution-grown C<sub>70</sub> crystals with rhombohedral shapes are shown in Fig. 3. For reference, the XRD pattern of the sublimation-grown C<sub>70</sub> crystals is also shown in this figure. The PXRD pattern of the sublimation-grown crystals can be explained in terms of two types of crystal forms: the rhombohedral form with  $a = 10.15$  Å and  $c = 27.95$  Å and the hexagonal form with  $a = 10.16$  Å and  $c = 18.6$  Å.

The difference between the two crystal forms is related to changes in the stacking order of the crystal planes. These crystal forms are also in good agreement with those previously reported.<sup>30–32</sup>

The pattern of solution-grown C<sub>70</sub> crystals with rhombohedral shapes is clearly different from that of sublimation-grown C<sub>70</sub> crystals. It is assigned to the hexagonal structure with lattice constants of  $a = 50.3013$  Å and  $c = 24.5686$  Å. This was also confirmed by SCXRD measurements. Notably, the XRD pattern remains unchanged even after annealing at 100 °C. This indicates that the hexagonal solvated structure is maintained even after annealing at 100 °C. Thus, the behavior of the XRD pattern is consistent with that of the FT-IR and TG results.

### Directly grown C<sub>70</sub> crystal FETs

Fig. 4(a) shows an SEM image of a C<sub>70</sub> single crystal with rhombohedral shapes grown directly on the FET substrate (direct-growth C<sub>70</sub> crystal FETs), which was used for the FET measurements in this study. The channel length  $L$  and the channel width  $W$  of the FET are estimated to be 23.1 μm and 26.1 μm, respectively (Fig. 4(a)).

An optical microscopy (OM) image of the direct-growth C<sub>70</sub> crystal FET is shown in Fig. S6 (ESI<sup>†</sup>). 75% of the obtained

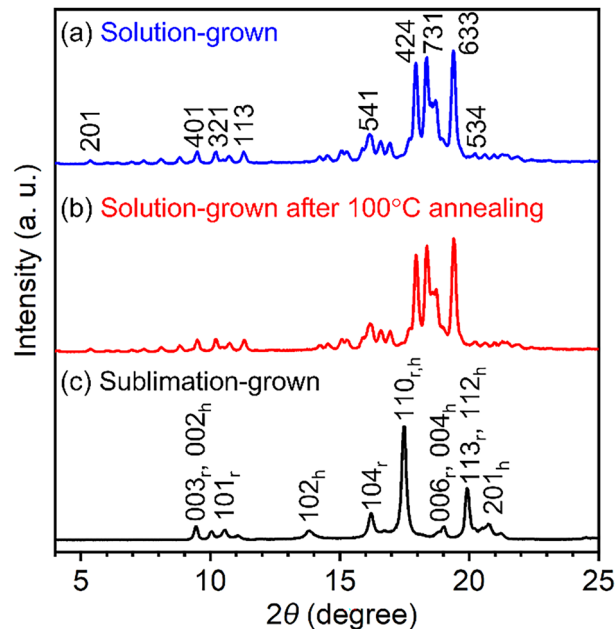


Fig. 3 PXRD patterns of C<sub>70</sub> crystals with rhombohedral shapes grown from C<sub>70</sub>-*m*-xylene solution. (a) and (b) XRD patterns after drying them in air for one day and after annealing them at 100 °C for 11 days under  $3.0\text{--}4.0 \times 10^{-3}$  Pa, respectively. As a reference, the XRD patterns of sublimation-grown C<sub>70</sub> crystals without the solvent is also shown as (c) in the figure. The XRD pattern of sublimation-grown C<sub>70</sub> crystals is understood by using those in two kinds of crystal forms such as rhombohedral (denoted as r) and hexagonal (denoted as h) forms.

rhombohedral crystals were grown to bridge the two electrodes on the substrate. In addition, the growth direction to bridge the two electrodes was always a defined crystallographic direction as shown in Fig. 4(a) and Fig. S6 (ESI<sup>†</sup>). The size distribution of the C<sub>70</sub> crystals grown to bridge the two electrodes is shown in Fig. S7(a) and (b) (ESI<sup>†</sup>), where the sizes correspond to the diagonal lengths (short and long) in the obtained crystal morphology as shown in Fig. S7(c) (ESI<sup>†</sup>). The short diagonal length, which corresponds to the bridge between the two electrodes, was relatively uniform with a size of  $51.0 \pm 8.80$  μm. For FET measurements, some rhombohedral crystals that bridged the two electrodes securely were left on the substrate, while others that bridged the two electrodes fairly well were removed from the substrate. To evaluate mobility, the channel width ( $W$ ) of all residual crystals bridging the two electrodes was measured from SEM images, as shown in Fig. 4(a).

Fig. 4(b) shows the output characteristics of the vacuum-dried FET. The source–drain current ( $I_{\text{DS}}$ ) increases linearly with the source–drain voltage ( $V_{\text{DS}}$ ) up to approximately  $V_{\text{DS}} = 15$  V and approaches a constant maximum value. The transfer characteristics at  $V_{\text{DS}} = 40$  V also exhibit good gate modulation with respect to the gate voltage ( $V_{\text{G}}$ ) (Fig. 4(c)). The output and transfer characteristics show typical n-type FET behavior. Analysis of the transfer characteristics at  $V_{\text{DS}} = 40$  V (Fig. 4(c)) shows that the electron mobility ( $\mu$ ), threshold voltage ( $V_{\text{T}}$ ) and on/off ratio ( $I_{\text{on}}/I_{\text{off}}$ ) of the direct growth C<sub>70</sub> crystal FET are estimated to be  $1.19 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, 15.9 V, and 39.6, respectively.



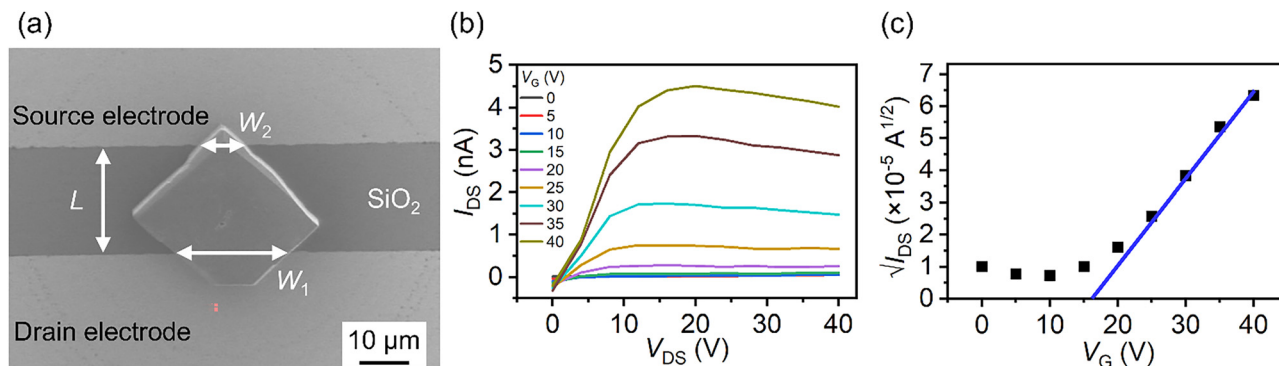


Fig. 4 (a) SEM image of a  $C_{70}$  crystal with a rhombohedral shape grown directly on and the electrode FET substrate from a  $C_{70}$ -*m*-xylene solution. Typical (b) output and (c) transfer characteristics of direct growth  $C_{70}$  crystal FETs before annealing in a vacuum, as measured at 27 °C.

Thus, the transport properties of the direct-growth  $C_{70}$  crystal FETs were successfully characterized.

The transport properties of  $C_{60}$  and  $C_{70}$  crystals are known to deteriorate significantly due to the adsorption of  $H_2O$  and  $O_2$  in the crystals; however, these species can be desorbed by annealing at approximately 100 °C.<sup>33,34</sup> To remove the  $H_2O$  and  $O_2$  adsorbed in the  $C_{70}$  crystals, the FET devices were annealed at 100 °C under  $3.0\text{--}4.0 \times 10^{-3}$  Pa for 25 days. Notably, the *m*-xylene in the solvated  $C_{70}$  crystals remains in the crystals even after vacuum-annealing at 100 °C, as the desorption of *m*-xylene requires a higher temperature of 140–165 °C, as shown in the FT-IR and TG results. The electron mobility in the direct growth  $C_{70}$  crystal FETs increased significantly by vacuum-annealing at 100 °C. This indicates that the increase in electron mobility is attributed to the desorption of  $H_2O$  and  $O_2$  by vacuum-annealing at 100 °C, as previously reported for  $C_{60}$  and  $C_{70}$  crystals.<sup>7,23</sup>

In addition, the effect of *m*-xylene in the solvated crystals is of interest for higher mobility. Evaporation of the solvent by heat-treatment at a higher temperature of 200 °C could lead to experimental evidence of solvent effects for solvated crystal FETs. However, heat treatment not only evaporates the solvent but also leads to the degradation of crystallinity with a change in the crystal structure as has already been observed for  $C_{70}$

needle crystals.<sup>23</sup> Therefore, it is difficult to accurately measure the solvent effect or pure  $C_{70}$  crystal FETs.

Fig. 5(a) shows the relationship between the electron mobility of the directly grown  $C_{70}$  crystal FETs and the number of days they were annealed at 100 °C in a vacuum, where the values of the electron mobilities were measured at 100 °C. The electron mobility increased and approached a constant maximum value as the number of days of annealing increased. The maximum value of mobility was  $1.50 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  after 25 days of annealing at 100 °C.

It is assumed that the mobility value reaches a constant maximum value after 25 days of annealing, although further annealing could lead to a slight increase in mobility. In fact, the dependence of the slope ( $\partial\sqrt{I_{DS}}/\partial V_G$ ) of the transfer characteristics, which is used to evaluate the mobility, on the number of annealing days was well-fitted with an exponential curve as shown in Fig. S8 (ESI<sup>†</sup>). After fitting, the constant maximum value of mobility is evaluated as  $1.59 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , which is slightly higher than the value after 25 days of annealing. A similar behavior of mobility as a function of the number of days of annealing was also observed for other samples with rhombohedral crystals. The saturation of mobility occurs in all samples after more than 20 days of annealing, where  $O_2$  and  $H_2O$  in the crystals are completely removed by annealing. The

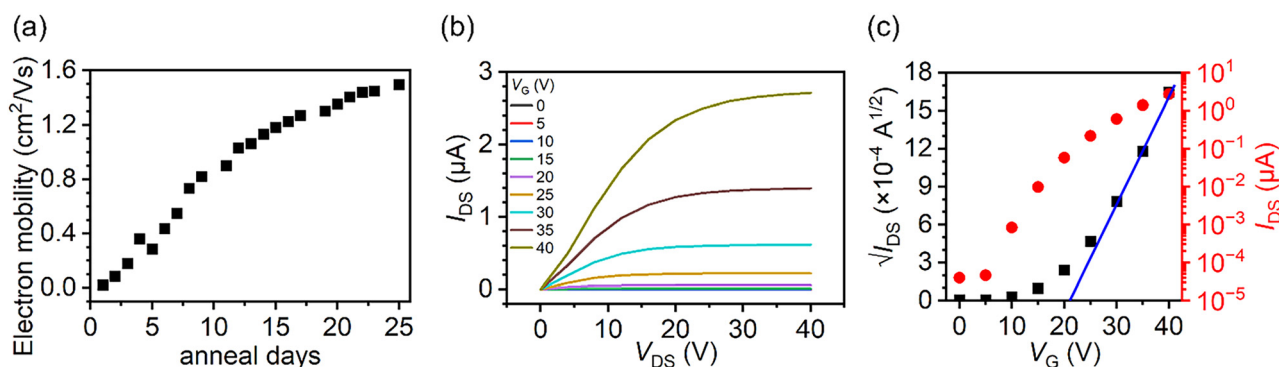


Fig. 5 (a) Increase in the electron mobility of direct growth  $C_{70}$  crystal FETs as a function of the number of days they were annealed at 100 °C under  $3.0\text{--}4.0 \times 10^{-3}$  Pa. Vacuum annealing leads to the desorption of  $H_2O$  and  $O_2$  adsorbed in the crystals. Typical (b) output and (c) transfer characteristics of direct growth  $C_{70}$  crystal FETs after annealing at 100 °C under  $3.0\text{--}4.0 \times 10^{-3}$  Pa for 25 days, as measured at 27 °C.



Table 1 Comparison of the electrical properties of fullerene-based OFETs reported to date

		Configuration	$\mu$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	$V_T$ (V)	$I_{on}/I_{off}$	Ref.
C <sub>60</sub>	Thin film	Bottom contact	8.00 × 10 <sup>-2</sup>	15.0	1.09 × 10 <sup>6</sup>	1
			5.60 × 10 <sup>-1</sup>	17.0	>10 <sup>8</sup>	3
			6.50 × 10 <sup>-1</sup>	32.0	>10 <sup>6</sup>	4
			2.00 × 10 <sup>-1</sup>	—	—	5
			3.23	17.1	4.00 × 10 <sup>6</sup>	6
			4.90	—	—	12
	Crystal	Bottom contact	6.00	—	—	5
			4.30	<1.00	>10 <sup>6</sup>	13
			3.00 × 10 <sup>-2</sup>	3.30 × 10 <sup>-1</sup>	1.35 × 10 <sup>2</sup>	7
			2.00 × 10 <sup>-2</sup>	0	—	8
			~ 10 <sup>-2</sup>	-13.0	~ 10 <sup>2</sup>	9
		Top contact	2.00 × 10 <sup>-3</sup>	—	—	10
			3.82 × 10 <sup>-2</sup>	—	—	11
			11.1	28.0	2.50 × 10 <sup>6</sup>	14
			2.00 ± 0.61	36.0 ~ 85.0	>10 <sup>6</sup>	15
			2.30	16.5	2.40 × 10 <sup>4</sup>	16
			5.09	6.60 × 10 <sup>-1</sup>	10 <sup>5</sup> -10 <sup>6</sup>	17
C <sub>70</sub>	Thin film	Bottom contact	2.00 × 10 <sup>-3</sup>	27.0	—	2
			6.60 × 10 <sup>-2</sup>	40.0	>10 <sup>5</sup>	4
	Crystal	Bottom contact	6.00 × 10 <sup>-5</sup>	—	—	22
			1.32 × 10 <sup>-2</sup>	9.64	64.0	23
			8.20 × 10 <sup>-5</sup>	—	—	20
			~ 10 <sup>-5</sup>	—	—	21
			1.14	17.2	7.84 × 10 <sup>4</sup>	This work

evaporation rate of O<sub>2</sub> and H<sub>2</sub>O is high in smaller crystals as the specific surface area is large in smaller crystals. More than 20 days of annealing for rhombohedral crystals is clearly longer than 9 days for smaller needle crystals reported previously.<sup>23</sup> Thus, the days of annealing leading to mobility saturation depend on the crystal size, *i.e.*, the specific surface area.

Fig. 5(b) and (c) show the output and transfer characteristics of the direct growth C<sub>70</sub> crystal FETs at 27 °C after annealing at 100 °C under 3.0–4.0 × 10<sup>-3</sup> Pa for 25 days. The current values of the  $\mu$ A orders increase sharply compared to the nA orders before annealing as shown in Fig. 4(b). According to previous studies on C<sub>70</sub> needle-crystal FETs with poor electrical contact between crystals and electrodes, in the output characteristics,  $I_{DS}$  increased non-linearly and slowly with  $V_{DS}$  in the low voltage range.<sup>25</sup> In addition, no current saturation was observed even at high  $V_{DS}$ . This behavior may be attributed to poor contact or non-ohmic contact between the C<sub>70</sub> crystal and the FET substrate with the electrodes. In the direct-growth C<sub>70</sub> crystal FETs measured in this study, the non-ohmic behavior was largely improved so that ideal and excellent output characteristics, including the linear and saturation regions, were clearly observed (Fig. 5(b)). The electron mobility,  $V_T$  and  $I_{on}/I_{off}$  of the direct growth C<sub>70</sub> crystal FETs after annealing are estimated to be 1.14 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, 21.1 V and 6.75 × 10<sup>4</sup>, respectively, as measured at 27 °C. The electron mobility increased by three orders of magnitude compared to that before annealing.

The electron mobility,  $V_T$ , and  $I_{on}/I_{off}$  for fullerene-based OFETs with C<sub>60</sub> are summarized in Table 1. The electron mobility of the direct-growth C<sub>70</sub> crystal FETs measured in this study exhibits the highest value compared to those of OFETs based on C<sub>70</sub> as previously reported.<sup>20–23</sup> The electron mobility value is also comparable to that of top-contact C<sub>60</sub> based FETs, which correspond to the highest performance in n-type OFETs.

The electron mobility values after annealing for 25 days were 1.50 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> at 100 °C and 1.14 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> at 27 °C, indicating that the mobility increases with temperature. This behaviour suggests that electron transport in the C<sub>70</sub> crystals follows a hopping conduction mechanism associated with thermal activity, which is a typical conduction mechanism in molecular crystals.

In previous studies on C<sub>70</sub> needle-crystal FETs, the electron mobility was estimated from the transfer characteristics, assuming negligible contact resistance between the C<sub>70</sub> crystal and the S/D electrodes on the substrate. However, if the contact resistance is significant, this may result in reduced current values, possibly leading to an underestimation of electron mobility. In contrast, in this study, the contact was significantly improved, minimizing the limit of the injection current and allowing a more accurate estimation of the intrinsic electron mobility.

## Conclusions

In this study, high-mobility FETs fabricated by the direct growth of C<sub>70</sub> crystals from C<sub>70</sub> saturated *m*-xylene solution have been demonstrated. Good electrical contact between the C<sub>70</sub> crystals and FET substrates was realized with electrodes in the bottom-gated bottom-contact FET configuration. The C<sub>70</sub> crystals obtained exhibit rhombohedral shapes with solvated hexagonal structures. Directly grown C<sub>70</sub> crystal FETs exhibit typical n-type output and transfer characteristics. The electron mobility increases with annealing at 100 °C in a vacuum, leading to the desorption of H<sub>2</sub>O and O<sub>2</sub> in the crystals, although solvation in the crystals is maintained. The solvated C<sub>70</sub> crystal FETs have a high electron mobility of 1.14 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> which is an improvement of more than two orders of magnitude compared to the previously reported



C<sub>70</sub> FETs. The electron mobility value was also comparable to that of the electron mobility in top-contact C<sub>60</sub> based FETs, which corresponds to the highest mobility in n-type OFETs. This shows the potential application of C<sub>70</sub> crystals in electronic devices. It is anticipated that more advanced solution-processing techniques developed for organic crystalline FETs<sup>24,25</sup> will be employed in the fabrication of high-mobility C<sub>70</sub> FETs for practical applications.

## Author contributions

Yuto Sakai: data curation, formal analysis, investigation, methodology, validation, visualization, writing review, and editing. Taiyo Araki: data curation, formal analysis, investigation, methodology, validation, visualization, writing review, and editing. Ryo Suzuki: data curation, formal analysis, funding acquisition, visualization, writing review, and editing. Toshiyuki Sasaki: data curation, formal analysis, visualization, writing review, and editing. Kouhei Ichihyanagi: data curation, formal analysis, visualization, writing review, and editing. Tadahiko Hirai: formal analysis, visualization, writing review, and editing. Nobuyuki Aoki: resources (FET devices), writing review, and editing. Masaru Tachibana: conceptualization, project administration, supervision, funding acquisition, writing – original draft, writing – review, and editing.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the ESI.†

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