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# Solvent-free Toner Printing of Organic Semiconductor Layer in Flexible Thin-film Transistors

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A solvent-free printing process for printed electronics was successfully developed using toner-type patterning of organic semiconductor toner particles and subsequent thin-film formation. These processes use the same principle as that used for laser printing. The organic thin-film transistors were prepared by electrically distributing the charged toner onto a Au electrode on a substrate film followed by thermal lamination. The thermal lamination was effective for obtaining an oriented and crystalline thin film. Toner printing is environmentally friendly compared with other printing technologies because it is solvent free, saves materials, and enables easy recycling. In addition, this technology simultaneously enables both wide-area and high-resolution printing.

keywords: printed electronics, flexible electronics, solvent-free, xerography, organic semiconductors

## I. INTRODUCTION

Wearable electronic devices are presently being developed mainly in the sports and healthcare fields. Although such wearable devices are expected to have an effect on future daily lifestyles, they must first become more lightweight and flexible. Methods for printing flexible electronics[1–11] on plastic films are being developed all over the world. In conventional printing methods, special inks including organic semiconductors and solvents are used. It is necessary for the solvents used in these special inks to dissolve the organic semiconductors in sufficient concentrations and to maintain the optimum viscosity for each printing method, such as inkjet and photogravure printing. Because many solvents for printed electronics have disadvantages, such as flammability, toxicity, and carcinogenicity, their use is regulated by international emission regulations[12, 13]. The emission of not only the solvents but also their vapors is difficult to regulate because the emission sources are widely dispersed from small offices to large factories; therefore, atmospheric pollution due to volatile organic compounds (VOCs) is a worldwide issue [14–25]. VOCs in the atmosphere generate photochemical smog through photochemical reactions that occur under ultraviolet light irradiation.

Our research group has developed an alternative printing method for printed electronics without using inks. Although inkjet and other printers designed for printed electronics are already commercially available, solvent-free printing is not. We previously developed a solvent-free thin-film fabrication process that involves thermal pressing[26], thermal lamination[27, 28], and ultrasonic

welding[29]. A thermal press was developed to prepare thin films of organic materials by thermally compressing the organic materials with two planar clamps[26]. Next, a thermal lamination method was developed by replacing the thermal planar press with thermal rollers for thin-film formation with a roll-to-roll scheme[27, 28]. Ultrasonic welding is a method used to fabricate organic thin films based on the local and instantaneous heating generated at the interface by the application of ultrasonic vibration[29]. In ultrasonic welding, it is not necessary to raise the temperature of the entire sample; therefore, it is possible to use plastic films whose melting points are lower than that of the organic semiconductor. These thin-film fabrication methods are solvent free, and the organic materials used in these methods are applicable to zone melting for ultrapure organic semiconductors[30–39]. However, these thin-film fabrication processes lack a patterning method for organic semiconductors. Therefore, in this work, we have developed a solvent-free patterning method of the organic thin film using toner-type printing, which is combined with thermal lamination[27, 28] to fabricate a thin-film transistor (TFT). The combination of toner-type patterning and subsequent thermal lamination is the same process as that used in laser printers.

## II. EXPERIMENTAL SECTION

Two substrates were prepared using the same procedures described in our previous work[26–29]. The first substrate was a thin hybrid polyimide film (POMI-RAN N) provided by Arakawa Chemical Industries, Ltd., Japan. The 12- $\mu\text{m}$ -thick hybrid polyimide film consisted of a 900-nm-thick parylene-SR ( $\epsilon_r = 3.34$ ) buffer layer and Au contact electrodes. The Au contact electrodes were thermally evaporated using a shadow mask, and the channel length and width were 20  $\mu\text{m}$  and 3.5 mm, respectively. The Au contact electrodes were chemically

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treated with pentafluorobenzenethiol to reduce the contact resistance[40–44]. This substrate is called the base film in this work. The second substrate was a thin POMIRAN N film, also 12  $\mu\text{m}$  thick, with a Au gate electrode and 900-nm-thick parylene-SR gate-insulating layer. This substrate is called the cover film in this work. The base and cover films had a symmetric material arrangement to cancel out internal compressive and tensile stresses at the organic layers when bending[45–49]. A small amount of dioctylbenzothienobenzothiophene ( $\text{C}_8\text{-BTBT}$ )[50–65] toner particles were electrically transferred onto the Au electrode on the base film with toner-type patterning. The toner pattern is determined by the two electrodes that attract the toner during printing. The TFT channel is formed by toner that spreads during the lamination that follows. After the toner patterning, the base film was covered with the cover film. The pair of POMIRAN N films, including the organic powder between them, was then inserted into a thermal laminator to fabricate the  $\text{C}_8\text{-BTBT}$  thin film.

### III. PREPARATION OF ORGANIC SEMICONDUCTOR TONER AND PRINCIPLE OF ELECTROSTATIC TRANSFER

Conventional toner used in commercial xerography is a mixture of pigments, plastics, wax, and charge control agents to achieve an appropriate electrical charge. However, chemical impurity is undesirable for the toner used in the printing of organic semiconductor layer because it affects the electronic properties of the organic semiconductor. Therefore, a pure organic semiconductor toner was prepared without additional chemical agents. Attempts were made to prepare organic toner particles with dioctylbenzothienobenzothiophene ( $\text{C}_8\text{-BTBT}$ ), dinaphthothienobenzothiophene, and 6,13-bis(triisopropylsilylethynyl)pentacene. Here, we focus on the results obtained with the  $\text{C}_8\text{-BTBT}$  toner. Figure 1(a) shows that the as-received  $\text{C}_8\text{-BTBT}$  powder was initially a protean granular powder with particle diameters of 50–200  $\mu\text{m}$ . This powder was confined in a plastic capsule with an appropriate amount of zirconia balls (1-mm diameter) and then milled in a ball-milling machine at 4500 rpm for 5 min. Figure 1(b) presents a scanning electron microscopy (SEM) image of the ground  $\text{C}_8\text{-BTBT}$  powder. The particle diameter of the ground  $\text{C}_8\text{-BTBT}$  powder ranges from less than 5 to 20  $\mu\text{m}$ . Detailed examination of the individual particles confirmed that the large particles included both aggregates of smaller toner particles and large single particles. The large particles are not suitable for toner printing; however, toner particles that are too large will spontaneously be excluded during the subsequent toner-type patterning process. In the next step, the toner particles were frictionally charged by mixing plastic-coated ferrite particles with diameters of approximately 60–100  $\mu\text{m}$ . These ferrite particles are called carrier particles. The role of the carrier

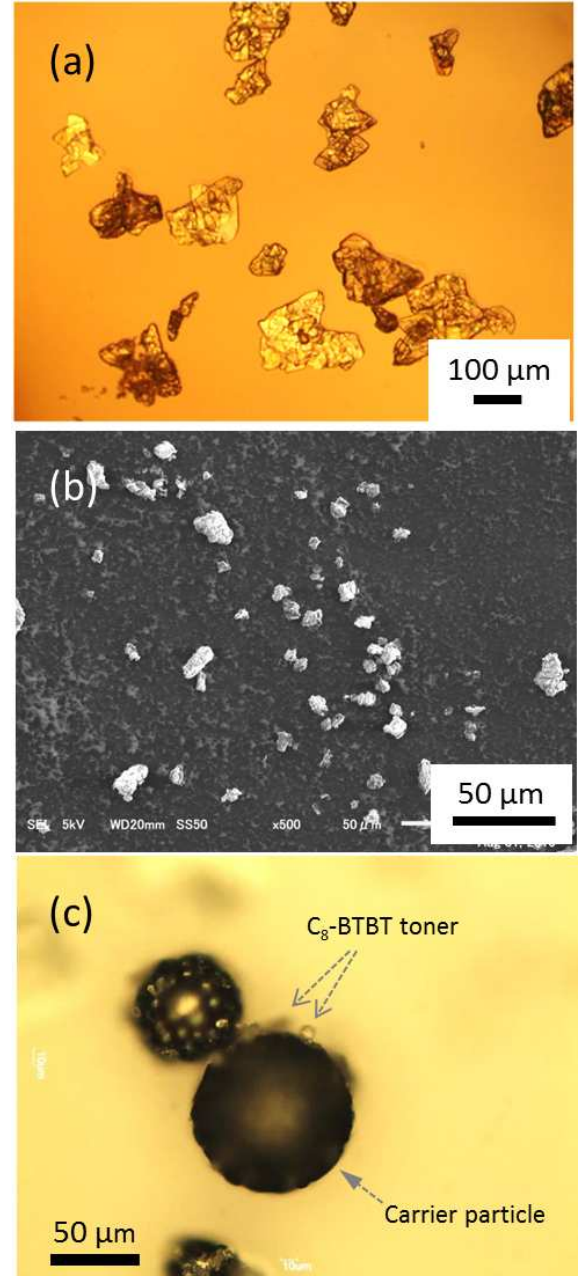


FIG. 1. (a) Optical micrograph of as-received dioctylbenzothienobenzothiophene ( $\text{C}_8\text{-BTBT}$ ) powder. Protean granular crystals with diameters of 50–200  $\mu\text{m}$  are observed. (b) Scanning electron microscopy image of ground  $\text{C}_8\text{-BTBT}$  powder. (c) Optical micrograph of the mixed carrier and  $\text{C}_8\text{-BTBT}$  toner particles.

particles was to induce and maintain an electrical charge on the toner particles. A set of purchased carrier particles includes two types of carrier particles to prepare negatively charged toner particles (N-01 carrier) and positively charged toner particles (P-02 carrier). Figure 1(c) presents an optical micrograph of the carrier and  $\text{C}_8\text{-BTBT}$  toner particle mixture. The spherical particles with diameters of 60–100  $\mu\text{m}$  are the carrier particles,

and the C<sub>8</sub>-BTBT toner appears as small particles adhered on the carrier particle. The C<sub>8</sub>-BTBT toner particles have an electrical charge of  $q_{\text{toner}}$  generated by frictional charging with the carrier particle surface. Thus, the C<sub>8</sub>-BTBT toner particles adhered on the surfaces of the carrier particle by van der Waals (vdW) and image forces because the carrier particles consist of conductors. These adhesion forces between the toner and carrier particles are discussed later.

Figure 2(a) presents a schematic illustration of the electrostatic transfer of the toner particle toward a flexible film substrate. The mixed particles obtained are fixed by a magnet because the carrier particles are composed of ferrite. When an external DC electric field ( $E$ ) is applied between the magnet and Au electrodes prepared on the flexible film surface, the charged toner particles are attracted by the electrostatic force. Figure 2(b) presents a schematic illustration of the adhesion force of the toner particle on the carrier particle surface. When a toner particle adhered on a carrier particle surface has an electric charge of  $q_{\text{toner}}$ , the image force is induced as an attractive Coulomb force between the real charged particle and image charge. The image charge is a virtual charge of  $-q_{\text{toner}}$  and is assumed to be located at the mirror position of the real charge toward the conductor surface plane. When we define the radius of the toner particle as  $r$ , the nominal distance from the charged toner particle to the image charge is  $2r$ . Therefore, the image force is proportional to  $q_{\text{toner}}^2/(2r)^2$ . In contrast, the vdW force originates from the London dispersion force and does not depend on  $q_{\text{toner}}$ . Therefore, the total adhesion force between the carrier and toner particle is expressed as

$$F_{\text{adhesion}} = (\text{vdW force}) + \frac{q_{\text{toner}}^2}{4\pi\epsilon(2r)^2},$$

where  $\epsilon$  is the dielectric constant of the atmosphere. To separate the toner particle from the surface of the carrier particle and allow transfer of the toner particle onto the Au electrode, an external electric field is applied between the magnet and Au electrode. The external electrostatic force on the toner particle is  $q_{\text{toner}}E$ , which pulls the toner particle from the surface of the carrier particle. Therefore, the total force affecting the toner particle is expressed as

$$F_{\text{total}} = (\text{vdW force}) + \frac{q_{\text{toner}}^2}{16\pi\epsilon r^2} - q_{\text{toner}}E.$$

Figure 2(c) shows the relationship between the adhesive force and external electrostatic force that affects a toner particle. When the external electrostatic force exceeds the adhesion force, the toner particle is separated from the surface of the carrier particle and transferred along the electric field toward the Au electrode pattern prepared on the flexible film substrate surface. Therefore, an external electric field of  $E_2$ , as shown in Figure 2(c), can transfer toner particles over a wide range of charge

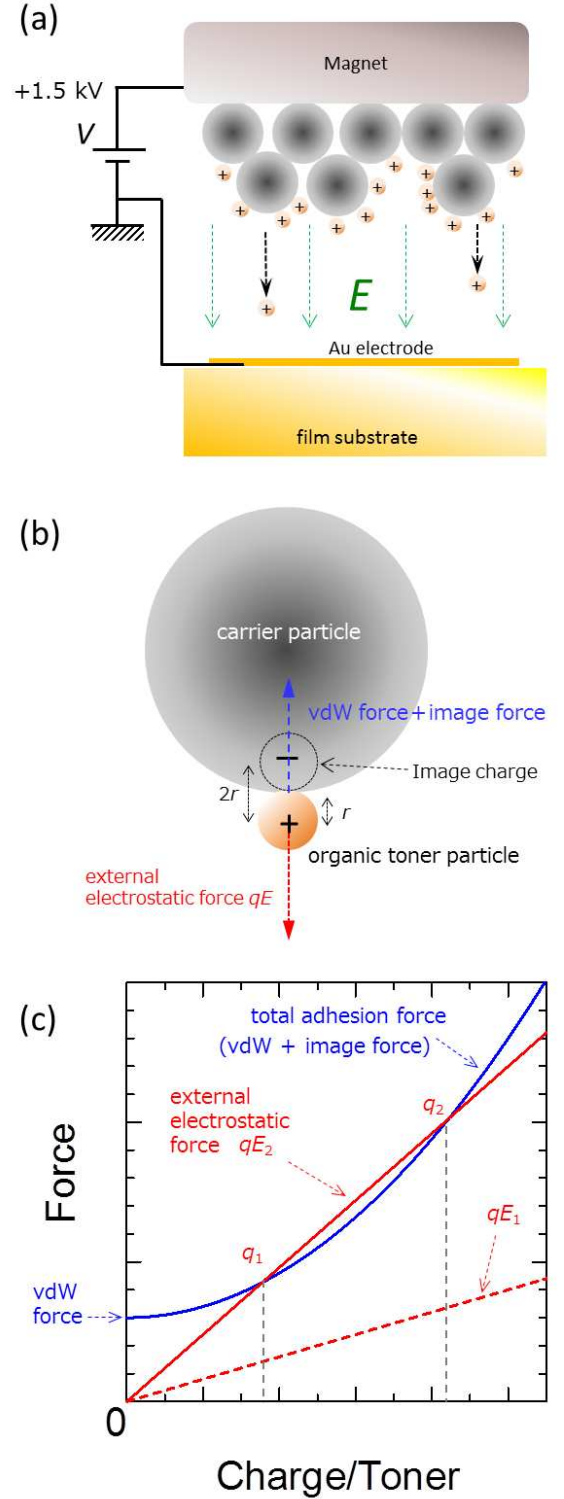


FIG. 2. (a) Schematic illustration of the electrostatic transfer of a toner particle from the surface of a carrier particle to the substrate. (b) Magnified view of a toner particle adhered on the surface of a carrier particle. The adhesion force of the toner particle on the carrier particle and the external electrostatic force needed to separate the organic toner from the carrier particle surface are indicated. (c) Relationship between the adhesion force and external electrostatic force that affects a charged toner particle.



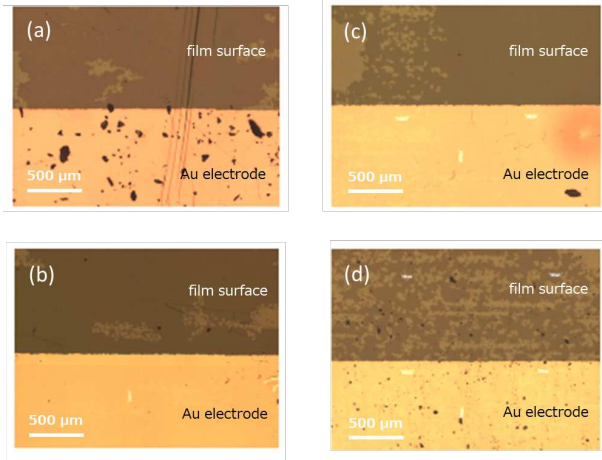


FIG. 3. Optical micrographs of electrostatic transfer of diocetylbenzothienobenzothiophene toner particles to the Au electrode using (a) N-01 carrier particles with 1.5 kV applied to the Au electrode and a grounded magnet; (b) N-01 carrier particles with 1.5 kV applied to the magnet; (c) P-02 carrier particles with 1.5 kV applied to the Au electrode; and (d) P-02 carrier particles with 1.5 kV applied to the magnet.

between  $q_1$  and  $q_2$ . In contrast, with an insufficient electric field (e.g.,  $E_1$  in Figure 2(c)), no toner particle is separated from the carrier particle surface. Therefore, there is a threshold electric field for electrostatic toner transfer. In addition, weakly charged toner particles cannot be transferred because of the lack of external force, and very highly charged toner particles also cannot be transferred because of the excess adhesive image force, even under a high electric field. After the separation of toner particles, the carrier particles remain on the magnet because they are strongly attracted by the magnetic force. In addition, there is no residual charge in the toner particle after the electrostatic transfer onto the Au electrode surface because the frictional charge in the toner particle promptly run from the toner particle to ground through the Au electrode.

#### IV. ELECTROSTATIC TONER PATTERNING AND DEVICE CHARACTERISTICS

Figure 3 shows the results of electrostatic toner transfer onto the POMIRAN N film substrates. These optical micrographs show the region around the edge of the Au electrode evaporated onto the POMIRAN N film surface. The lower half of each micrograph shows the surface of the thin Au electrode prepared on the film surface, and the upper half shows the surface of the substrate film. When N-01 carrier particles that negatively charge the toner particles were used, the C<sub>8</sub>-BTBT toner particles were expected to be negatively charged. Therefore, when a positive voltage was applied to the Au electrodes and the magnet was electrically grounded, the C<sub>8</sub>-BTBT toner particles were transferred from the surface of the

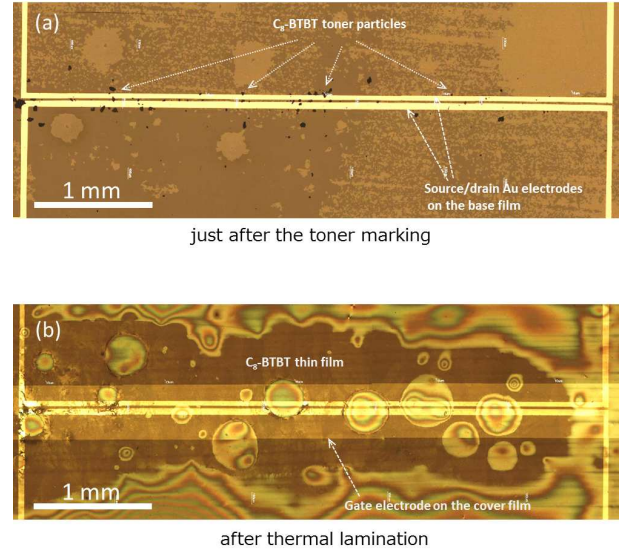


FIG. 4. Wide-range optical micrograph of (a) electrostatic toner transfer using diocetylbenzothienobenzothiophene (C<sub>8</sub>-BTBT) toner, whereby C<sub>8</sub>-BTBT toner particles are distributed around the Au electrodes, and (b) organic thin-film transistor after thermal lamination.

carrier particles toward the surface of the Au electrodes. In contrast, when a positive voltage was applied to the magnet and the Au electrodes were grounded, no C<sub>8</sub>-BTBT toner particles were expected to be transferred. Figure 3(a) and (b) present the corresponding results. Many toner particles were transferred onto the Au electrode surface, as observed in Figure 3(a), whereas almost no toner particles are observed in Figure 3(b). However, when P-02 carrier particles that make the toner particles positively charged were used, no C<sub>8</sub>-BTBT toner particles were transferred with the application of a positive voltage to the Au electrode (Figure 3(c)). If the electric field was inverted, then C<sub>8</sub>-BTBT toner particles were transferred onto the Au electrode, as observed in Figure 3(d). Therefore, we can conclude that the C<sub>8</sub>-BTBT toner can be selectively charged to be negative or positive by selecting the carrier particle type, which is very advantageous for the development of a toner-printing system.

Figure 4(a) shows the result of the electrostatic transfer of the C<sub>8</sub>-BTBT toner. Figure 4(a) is an optical micrograph of the POMIRAN N substrate (base film) surface directly after the electrostatic transfer of the organic semiconductor toner. The corresponding Au electrode pattern prepared on the substrate surface is observed. C<sub>8</sub>-BTBT toner particles are also observed near the Au electrodes. The organic semiconductor toner was selectively scattered around the Au electrodes. After the patterning, the cover film was placed on the base film, which was then inserted into a thermal laminator[27, 28]. The C<sub>8</sub>-BTBT toner particles were melted and spread by the heat and pressure applied in the thermal laminator

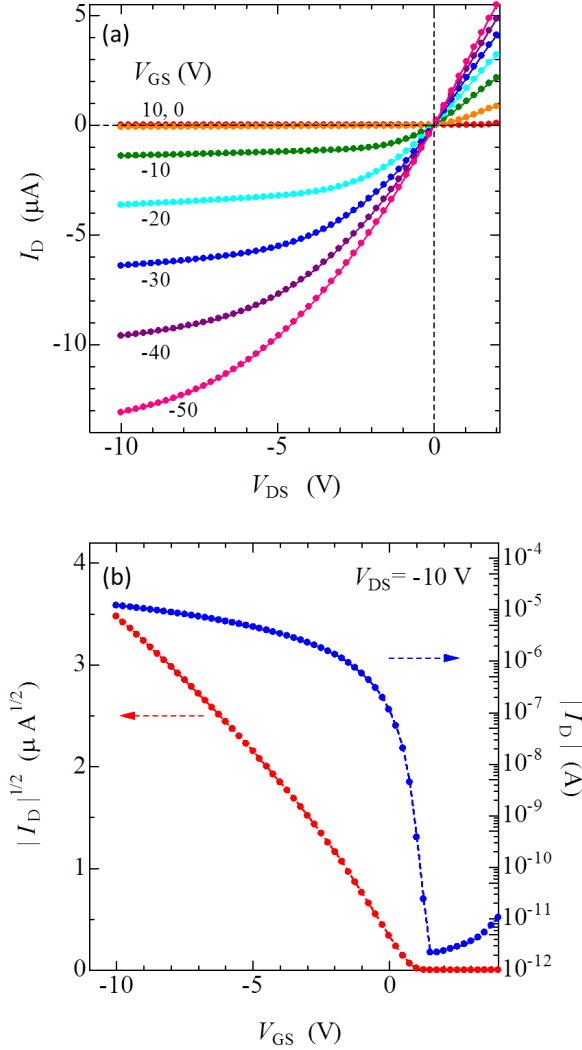


FIG. 5. (a) Output characteristics and (b) transfer characteristics of diocetylbenzothienobenzothiophene thin-film transistor fabricated by toner printing. In the figure,  $I_D$ ,  $V_{DS}$ , and  $V_{GS}$  represent the drain current, drain/source voltage, and gate/source voltage, respectively.

to form a thin film of C<sub>8</sub>-BTBT. Figure 4(b) presents an optical micrograph of the C<sub>8</sub>-BTBT TFT fabricated by toner-type patterning and subsequent thermal lamination, which is the same process performed in laser printers and Xerox machines. Laser printers and Xerox machines make patterns of toner particles on paper and then thermally fix the powder pattern to complete the printed document. We have clearly demonstrated that toner-type printing can be used to prepare flexible printed electronics without the need for solvents, which means that the printed electronics can be directly and digitally printed by laser printers.

In addition, several voids were sometimes observed in the thin film because of micrometer-sized dust particles in the atmosphere. The plastic film substrate easily at-

tracts residual dust particles in the atmosphere, even in a clean booth. A particle in each void can be seen in Figure 4(b) and the magnified micrograph (see Figure S1(a) in the Supplemental Material [66]). If dust particles are present between the base and cover film, voids are formed in the C<sub>8</sub>-BTBT thin film because the dust particles do not melt but instead raise the cover film up to the height of the dust particle diameter (several micrometers), creating an empty space between the base and cover film (see Figure S1(b) in the Supplemental Material [66]). In this situation, it is impossible for the C<sub>8</sub>-BTBT melt to fill the space created by the dust particle. Although this particle inclusion problem is common in printed electronics, it can be solved with various technical approaches.

Figure 5 presents the transfer characteristics of a C<sub>8</sub>-BTBT TFT fabricated by toner printing. p-type field-effect transistor characteristics were observed, and the typical field-effect hole mobility, threshold voltage, and subthreshold swing were 0.33 cm<sup>2</sup>/Vs, 1.5 V, and <250 mV/dec, respectively. These electronic properties are by no means inferior to OTFTs fabricated by conventional printing methods on plastic film substrates. In addition, the performance with aging was examined in ambient air and under repetitive bending up to 10,000 times (see Figure S2 in the Supplemental Material [67]). The OTFT kept initial electrical characteristics throughout the aging condition. Thermal lamination was demonstrated to be effective for obtaining an oriented and crystalline C<sub>8</sub>-BTBT thin film between the base and cover film without any post-deposition treatment [27, 28]. This TFT was very thin, and X-ray diffraction analysis revealed that the film was crystalline and that the *c*-axis was oriented normal to the substrate surface. In addition, lateral oriented growth effect due to the flow direction of the organic melt was observed in this method[27]. The advantage here is that organic flexible devices are fabricated using an environmentally friendly printing method.

## V. CONCLUSION

We have successfully developed a solvent-free printing process of organic semiconductor layer for printed electronics using a combination of toner-type patterning of organic toner particles and thermal thin-film formation. These processes involve the same principles as those used in laser printing. Toner printing is superior to other printing methods because it is solvent free, saves materials, and allows easy recycling, thereby reducing its environmental impact. In addition, both wide-area and high-resolution printing are simultaneously possible using toner-type printing. Printed integrated circuits such as complementary metal-oxide-semiconductor (CMOS) logic could also be printed using toner printing with multiple toner cartridges containing p-type and n-type semiconductors, insulating polymers, and conductive toners, similar to the principles used in color laser printers. Toner printing is also a direct and digital print-

ing process, similar to that used in 3D printers. 3D printers have enabled the innovation of prototyping; therefore, we expect that laser printers will be used to print organic flexible electronics in the future.

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- [1] F. G. del Pozo, S. Fabiano, R. Pfattner, S. Georgakopoulos, S. Galindo, X. Liu, S. Braun, M. Fahlman, J. Veciana, C. Rovira, X. Crispin, M. Berggren and M. Mas-Torrent, Single Crystal-Like Performance in Solution-Coated Thin-Film Organic Field-Effect Transistors, *Adv. Funct. Mater.* **26**, 2379 (2016).
  - [2] Y. Takeda, K. Hayasaka, R. Shiwaku, K. Yokosawa, T. Shiba, M. Mamada, D. Kumaki, K. Fukuda, and S. Tokito, Fabrication of Ultra-Thin Printed Organic TFT CMOS Logic Circuits Optimized for Low-Voltage Wearable Sensor Applications, *Sci. Rep.* **6**, 25714 (2016).
  - [3] K. Fukuda, T. Sekine, R. Shiwaku, T. Morimoto, D. Kumaki, and S. Tokito, Free-Standing Organic Transistors and Circuits with Sub-Micron Thicknesses, *Sci. Rep.* **6**, 27450 (2016).
  - [4] W. Xu, Z. Hu, H. Liu, L. Lan, J. Peng, J. Wang, and Y. Cao, Flexible All-organic, All-solution Processed Thin Film Transistor Array with Ultrashort Channel, *Sci. Rep.* **6**, 29055 (2016).
  - [5] X. Ren, K. Pei, B. Peng, Z. Zhang, Z. Wang, X. Wan, and P. K. L. Chan, A Low-Operating-Power and Flexible Active-Matrix Organic-Transistor Temperature-Sensor Array, *Adv. Mater.* **28**, 4832 (2016).
  - [6] L. T. Duy, T. Q. Trung, V. Q. Dang, B.-U. Hwang, S. Siddiqui, I.-Y. Son, S. K. Yoon, D. J. Chung, and N.-E. Lee, Flexible Transparent Reduced Graphene Oxide Sensor Coupled with Organic Dye Molecules for Rapid Dual-Mode Ammonia Gas Detection, *Adv. Funct. Mater.* **26**, 4329 (2016).
  - [7] U. Kraft, M. Sejfic, M. J. Kang, K. Takimiya, T. Zaki, F. Letzkus, J. N. Burghartz, E. Weber, and H. Klauk, Flexible Low-Voltage Organic Complementary Circuits: Finding the Optimum Combination of Semiconductors and Monolayer Gate Dielectrics, *Adv. Mater.* **27**, 207 (2015).
  - [8] M. Drack, I. Graz, T. Sekitani, T. Someya, M. Kaltenbrunner, and S. Bauer, An Imperceptible Plastic Electronic Wrap, *Adv. Mater.* **27**, 34 (2015).
  - [9] C. B. Park, K. M. Kim, J. E. Lee, H. Na, S. S. Yoo, and M. S. Yang, Flexible electrophoretic display driven by solution-processed organic TFT with highly stable bending feature, *Org. Electron.* **15**, 3538 (2014).
  - [10] H. Kang, R. Kitsomboonloha, K. Ulmer, L. Stecker, G. Grau, J. Jang, and V. Subramanian, Megahertz-class printed high mobility organic thin-film transistors and inverters on plastic using attoliter-scale high-speed gravure-printed sub-5 nm gate electrodes, *Org. Electron.* **15**, 3639 (2014).
  - [11] A. Sou, S. Jung, E. Gili, V. Pecunia, J. Joimel, G. Fichet, and H. Sirringhaus, Programmable logic circuits for functional integrated smart plastic systems, *Org. Electron.* **15**, 3111 (2014).
  - [12] C. Capello, U. Fischer, and K. Hungerbühler, What is a green solvent? A comprehensive framework for the environmental assessment of solvents, *Green Chem.* **9**, 927 (2007).
  - [13] T. Erdmenger, C. Guerrero-Sanchez, J. Vitz, R. Hoogenboom, and U. S. Schubert, Recent developments in the utilization of green solvents in polymer chemistry, *Chem. Soc. Rev.* **39**, 3317 (2010).
  - [14] J. Li, R. Wu, Y. Li, Y. Hao, S. Xie, and L. Zeng, Effects of rigorous emission controls on reducing ambient volatile organic compounds in Beijing, China, *Sci. Total Environ.* **557–558**, 531 (2016).
  - [15] S. Mukerjee, L. A. Smith, E. D. Thoma, K. D. Oliver, D. A. Whitaker, T. Wu, M. Colon, L. Alston, T. A. Cousett, and C. Stallings, Spatial analysis of volatile organic compounds in South Philadelphia using passive samplers, *J. Air Waste Manage. Assoc.* **66**, 492–498 (2016).
  - [16] F. Villanueva, A. Notario, A. Tapia, J. Albaladejo, B. Cabanas, and E. Martinez, Ambient levels of volatile organic compounds and criteria pollutants in the most industrialized area of central Iberian Peninsula: intercomparison with an urban site, *Environ. Technol.* **37**, 983–996 (2016).
  - [17] Q. He, Q. Song, Y. Yan, Z. Wang, L. Guo, and X. Wang, Exposure to Particle Matters and Hazardous Volatile Organic Compounds in Selected Hot Spring Hotels in Guangdong, China, *Atmosphere* **7**, 54 (2016).
  - [18] T. Tuomi and S. Vainiotalo, The guideline and target values for total volatile organic compound concentrations in industrial indoor environments in Finland, *Indoor Built Environ.* **25**, 424–434 (2016).
  - [19] M. A. K. Khalil, C. L. Butenhoff, W. C. Porter, M. Almazroui, A. Alkhalaf, and M. S. Al-Sahafi, Air quality in Yanbu, Saudi Arabia, *J. Air Waste Manage. Assoc.* **66**, 341–355 (2016).
  - [20] F. Wu, Y. Yu, J. Sun, J. Zhang, J. Wang, G. Tang, and Y. Wang, Characteristics, source apportionment and re-

- activity of ambient volatile organic compounds at Dinghu Mountain in Guangdong Province, China., *Sci. Total Environ.* **548-549**, 347–359 (2016).
- [21] P. Jaramillo and N. Z. Muller, Air pollution emissions and damages from energy production in the U.S.: 2002-2011, *Energy Policy* **90**, 202–211 (2016).
- [22] R. Wu, Y. Bo, J. Li, L. Li, Y. Li, and S. Xie, Method to establish the emission inventory of anthropogenic volatile organic compounds in China and its application in the period 2008-2012, *Atmos. Environ.* **127**, 244-254 (2016).
- [23] X.P. Lyu, N. Chen, H. Guo, W. H. Zhang, N. Wang, Y. Wang, and M. Liu, Corrigendum to "Ambient volatile organic compounds and their effect on ozone production in Wuhan, central China", *Sci. Total Environ.* **541**, 200–209 (2016).
- [24] M. Strum and R. Scheffe, National review of ambient air toxics observations, *J. Air Waste Manage. Assoc.* **66**, 120–133 (2016).
- [25] Y. Pang, M. Fuentes, and P. Rieger, Trends in selected ambient volatile organic compound (VOC) concentrations and a comparison to mobile source emission trends in California's South Coast Air Basin, *Atmos. Environ.* **122**, 686–695 (2015).
- [26] A. Inoue, T. Okamoto, M. Sakai, S. Kuniyoshi, H. Yamauchi, M. Nakamura, and K. Kudo, Flexible organic field-effect transistor fabricated by thermal press process, *Phys. Status Solidi A* **210**, 1353 (2013).
- [27] M. Sakai, T. Okamoto, Y. Yamazaki, J. Hayashi, S. Yamaguchi, S. Kuniyoshi, H. Yamauchi, Y. Sadamitsu, M. Hamada, and K. Kudo, Organic thin-film transistor fabricated between flexible films by thermal lamination, *Phys. Status Solidi RRL* **7**, 1093 (2013).
- [28] H. Ishii, K. Kudo, T. Nakayama, N. Ueno, *Electronic Processes in Organic Electronics* (Springer Series in Materials Science, Springer, 2015), Vol. 209, p. 161.
- [29] T. Sasaki, M. Sakai, T. Ko, Y. Okada, H. Yamauchi, K. Kudo, Y. Sadamitsu, and S. Shinamura, Solvent-Free Printing of Flexible Organic Thin Film Transistors by Ultrasonic Welding, *Adv. Electron. Mater.* **2**, 1500221 (2016).
- [30] I. H. Hong, K. J. Tan, M. Toh, H. Jiang, K. Zhang, and C. Kloc, Impurities in zone-refining anthracene crystals, *J. Cryst. Growth* **363**, 61 (2013).
- [31] Z. Wang, S. L. Hemmer, D. M. Friedrich, and A. G. Joly, Anthracene as the Origin of the Red-Shifted Emission from Commercial Zone-Refined Phenanthrene Sorbed on Mineral Surfaces, *J. Phys. Chem. A* **105**, 6020 (2001).
- [32] H. Jiang and C. Kloc, Single-crystal growth of organic semiconductors, *MRS Bulletin* **38**, 28 (2013).
- [33] C.-Y. Liu and A. J. Bard, In-Situ Regrowth and Purification by Zone Melting of Organic Single-Crystal Thin Films Yielding Significantly Enhanced Optoelectronic Properties, *Chem. Mater.* **12**, 2353 (2000).
- [34] N. Karl, Charge carrier transport in organic semiconductors, *Synthetic Metals* **133–134**, 649 (2003).
- [35] N. Karl and J. Marktanner, Electron and Hole Mobilities in High Purity Anthracene Single Crystals, *Mol. Cryst. Liq. Cryst.* **355**, 149 (2001).
- [36] N. Karl, K. H. Kraft, and J. Marktanner, Fast electronic transport in organic molecular solids?, *J. Vac. Sci. Technol.* **17**, 2318 (1999).
- [37] N. Karl, Growth and electrical properties of high purity organic molecular crystals, *J. Cryst. Growth* **99**, 1009 (1990).
- [38] N. Karl, Organic Semiconductors: Purification and Crystal Growth, *Mol. Cryst. Liq. Cryst.* **171**, 157 (1989).
- [39] W. Warta, R. Stehle, and N. Karl, Ultrapure, high mobility organic photoconductors, *Applied Physics A* **36**, 163 (1985).
- [40] M. Kitamura and Y. Arakawa, High Current-Gain Cut-off Frequencies above 10 MHz in n-Channel C60 and p-Channel Pentacene Thin-Film Transistors, *Jpn. J. Appl. Phys.* **50**, 01BC01 (2011).
- [41] M. Kitamura, Y. Kuzumoto, S. Aomori, and Y. Arakawa, High-Frequency Organic Complementary Ring Oscillator Operating up to 200 kHz, *Appl. Phys. Express* **4** 051601 (2011).
- [42] M. Kitamura, Y. Kuzumoto, W. Kang, S. Aomori, and Y. Arakawa, High conductance bottom-contact pentacene thin-film transistors with gold-nickel adhesion layers, *Appl. Phys. Lett.* **97**, 033306 (2010).
- [43] Y. Kuzumoto and M. Kitamura, Work function of gold surfaces modified using substituted benzenethiols: Reaction time dependence and thermal stability, *Appl. Phys. Express* **7**, 035701 (2014).
- [44] M. Kitamura, Y. Kuzumoto, and Y. Arakawa, Short-Channel, High-Mobility Organic Thin-Film Transistors with Alkylated Dinaphthothienothiophene, *Phys. Status Solidi C* **10**, 1632–1635 (2013).
- [45] T. Sekitani, S. Iba, Y. Kato, Y. Noguchi, T. Someya, and T. Sakurai, Ultraflexible organic field-effect transistors embedded at a neutral strain position, *Appl. Phys. Lett.* **87**, 173502 (2005).
- [46] M. Sakai, Y. Yamazaki, S. Yamaguchi, J. Hayashi, and K. Kudo, *Phys. Status Solidi A* **211**, 795 (2014).
- [47] Z. Suo, E.Y. Ma, H. Gleskova, and S. Wagner, Mechanics of rollable and foldable film-on-foil electronics, *Appl. Phys. Lett.* **74**, 1177 (1999).
- [48] M. Kanari, M. Kunimoto, T. Wakamatsu, and I. Ihara, Critical bending radius and electrical behaviors of organic field effect transistors under elastoplastic bending strain, *Thin Solid Films* **518**, 2764 (2010).
- [49] N. Kim and S. Graham, Development of highly flexible and ultra-low permeation rate thin-film barrier structure for organic electronics, *Thin Solid Films* **547**, 57 (2013).
- [50] H. Ebata, T. Izawa, E. Miyazaki, K. Takimiya, M. Ikeda, H. Kuwabara, and T. Yui, Highly Soluble [1]Benzothieno[3,2-b]benzothiophene (BTBT) Derivatives for High-Performance, Solution-Processed Organic Field-Effect Transistors, *J. Am. Chem. Soc.* **129**, 15732 (2007).
- [51] T. Uemura, Y. Hirose, M. Uno, K. Takimiya, and J. Takeya, Very High Mobility in Solution-Processed Organic Thin-Film Transistors of Highly Ordered [1]Benzothieno[3,2-b]benzothiophene Derivatives, *Appl. Phys. Express* **2**, 111501 (2009).
- [52] T. Endo, T. Nagase, T. Kobayashi, K. Takimiya, M. Ikeda, and H. Naito, Solution-Processed Diocylbenzothienobenzothiophene-Based Top-Gate Organic Transistors with High Mobility, Low Threshold Voltage, and High Electrical Stability, *Appl. Phys. Express* **3**, 121601 (2010).
- [53] M. Kano, T. Minari, and K. Tsukagoshi, All-Solution-Processed Selective Assembly of Flexible Organic Field-Effect Transistor Arrays, *Appl. Phys. Express* **3**, 051601 (2010).
- [54] K. Takimiya, S. Shinamura, I. Osaka, and E. Miyazaki, Thienoacene-Based Organic Semiconductors,



- Adv. Mater. **23**, 4347 (2011).
- [55] C. Liu, T. Minari, X. Lu, A. Kumatani, K. Takimiya, and K. Tsukagoshi, Solution-Processable Organic Single Crystals with Bandlike Transport in Field-Effect Transistors, Adv. Mater. **23**, 523 (2011).
  - [56] H. Minemawari, T. Yamada, H. Matsui, J. Tsutsumi, S. Haas, R. Chiba, R. Kumai, and T. Hasegawa, Inkjet printing of single-crystal films, Nature **475**, 364 (2011).
  - [57] J. Soeda, Y. Hirose, M. Yamagishi, A. Nakao, T. Uemura, K. Nakayama, M. Uno, Y. Nakazawa, K. Takimiya, and J. Takeya, Solution-Crystallized Organic Field-Effect Transistors with Charge-Acceptor Layers: High-Mobility and Low-Threshold-Voltage Operation in Air, Adv. Mater. **23**, 3309 (2011).
  - [58] H. Tanaka, M. Kozuka, S. I. Watanabe, H. Ito, Y. Shimoi, K. Takimiya, and S. I. Kuroda, Observation of field-induced charge carriers in high-mobility organic transistors of a thienothiophene-based small molecule: Electron spin resonance measurements, Phys. Rev. B **84**, 081306(R) (2011).
  - [59] Y. Li, C. Liu, A. Kumatani, P. Darmawan, T. Minari, and K. Tsukagoshi, Patterning solution-processed organic single-crystal transistors with high device performance, AIP Adv. **1**, 022149 (2011).
  - [60] T. Minari, C. Liu, M. Kano, and K. Tsukagoshi, Controlled Self-Assembly of Organic Semiconductors for Solution-Based Fabrication of Organic Field-Effect Transistors, Adv. Mater. **24**, 299 (2012).
  - [61] T. Minari, P. Darmawan, C. Liu, Y. Li, Y. Xu, and K. Tsukagoshi, Highly enhanced charge injection in thienoacene-based organic field-effect transistors with chemically doped contact, Appl. Phys. Lett. **100**, 093303 (2012).
  - [62] A. Kumatani, C. Liu, Y. Li, P. Darmawan, K. Takimiya, T. Minari, and K. Tsukagoshi, Solution-processed, Self-organized Organic Single Crystal Arrays with Controlled Crystal Orientation, Sci. Rep. **2**, 393 (2012).
  - [63] Y. Li, C. Liu, Y. Xu, T. Minari, P. Darmawan, and K. Tsukagoshi, Solution-processed organic crystals for field-effect transistor arrays with smooth semiconductor/dielectric interface on paper substrates, Org. Electron. **13**, 815 (2012).
  - [64] Y. Li, C. Liu, A. Kumatani, P. Darmawan, T. Minari, and K. Tsukagoshi, Large plate-like organic crystals from direct spin-coating for solution-processed field-effect transistor arrays with high uniformity, Org. Electron. **13**, 264 (2012).
  - [65] Y. Li, C. Liu, M.V. Lee, Y. Xu, X. Wang, Y. Shi, and K. Tsukagoshi, In situ purification to eliminate the influence of impurities in solution-processed organic crystals for transistor arrays, J. Mater. Chem. C **1**, 1352 (2013).
  - [66] See Supplemental Material at [] for the magnified optical micrograph of voids, and cross-sectional illustration of the void.
  - [67] See Supplemental Material at [] for transfer characteristics of OTFT with aging examined under ambient air condition and repetitive bending up to 10000 times.