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Introduction

Compared to amorphous and polycrystalline states, single crystals generally show much better performance as semiconductors in organic field effect transistors (OFETs).^{1–4} This phenomenon can be attributed to the fact that single crystals are free of grain boundaries and molecular disorder, and carrier migration between the localized states is not limited by the hopping mechanism, resulting in higher mobility.⁵ Therefore, the exploration of organic single crystals for device fabrication has attracted much attention.^{4,6–8} The organic single crystals were usually prepared by a vacuum vapor⁹ or solution method^{3,5,10} until the solvent vapor annealing (SVA) method^{11–13} was developed. The SVA method partially dissolves the semiconductor

Preparation of highly oriented single crystal arrays of C8-BTBT by epitaxial growth on oriented isotactic polypropylene[†]

Mingliang Li, ^(D) ^{ab} Tingcong Jiang,^c Xiaoge Wang,^d Hongliang Chen, ^(D) ^e Shuo Li,^{ab} Feng Wei,^{ab} Zhongjie Ren, ^(D) ^c Shouke Yan, ^(D) ^{*^c} Xuefeng Guo ^(D) ^{*df} and Hailing Tu^{*ab}

Device fabrication with organic single crystals is an important method for high device performance. High-quality organic semiconductor crystals are usually grown by a lab solution method, by which it is difficult to fabricate crystal arrays on the substrate, let alone achieve industrial production. Therefore, in this work, oriented single crystal arrays have been prepared by epitaxial growth. As an example, 2,7-dioctyl[1]benzothieno[3,2-*b*]benzothiophene (C8-BTBT) was spin-coated on the surface of a highly oriented melt-drawn isotactic polypropylene (iPP) film on 300 nm SiO₂ substrates as an auxiliary dielectric layer, and highly oriented arrays of C8-BTBT single crystals are obtained by epitaxial growth in the solvent vapor annealing (SVA) approach. The devices based on the thus prepared C8-BTBT array have a yield of up to 81%, an average mobility of 2.5 cm² V⁻¹ s⁻¹, a maximum mobility of 9.3 cm² V⁻¹ s⁻¹ and an on/off ratio of 10⁷. Hence, our method facilitates the large-scale fabrication of highly oriented single crystal arrays with high quality, which will promote further industrial application.

molecules using saturated vapor, and at the same time the molecules can undergo a higher degree of self-assembly. Compared with thermal annealing¹⁴ in an ambient environment, the SVA method can obtain high-quality semiconductor single crystals more efficiently. However, the SVA method is usually suitable for the preparation of randomly distributed crystals. The preparation of large-scale¹⁵ and highly oriented single crystals¹⁶ remains a challenge. In this work, we report a way to prepare highly oriented single crystal arrays of 2,7-dioctyl[1]benzothieno[3,2-*b*]benzothiophene (C8-BTBT), a high-performance and stable semiconductor.¹⁷⁻¹⁹ To this end, we use a highly oriented melt-drawn isotactic polypropylene (iPP) film²⁰⁻²³ supported by 300 nm SiO₂ substrates as an auxiliary dielectric layer^{24,25} and the oriented substrate for the epitaxial growth of C8-BTBT.^{26,27} After spin coating a thin layer of C8-BTBT on the iPP covered substrate, highly oriented single crystal arrays of C8-BTBT with individual single crystals of up to 190 µm in length were obtained through the SVA method. It was found that the devices based on the thus prepared C8-BTBT arrays have a yield of up to 81% and an average mobility of 2.5 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The device with the best performance shows a maximum mobility of 9.3 cm² V⁻¹ s⁻¹ and an on/off ratio of 10⁷. This reveals that epitaxial growth on the oriented substrates provides an efficient way for largescale oriented single crystal device fabrication and industrial production.

^a GRIMAT Engineering Institute Co., Ltd, China

^b State Key Laboratory of Advanced Materials for Smart Sensing, General Research Institute for Nonferrous Metals, China

^c State Key Laboratory of Chemical Resource Engineering,

Beijing University of Chemical Technology, China

^d Beijing National Laboratory for Molecular Sciences, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, China. E-mail: guoxf@pku.edu.cn

^e Department of Chemistry, Northwestern University, USA

^f Department of Materials Science and Engineering, College of Engineering, Peking University, China

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Fig. 1 The fabrication process of the oriented organic single crystal array by epitaxial growth on the oriented iPP through SVA. (a) A cleaned substrate with 300 nm SiO_2 ; (b) attaching of a highly oriented iPP film on the substrate as an auxiliary dielectric layer; (c) solution of C8-BTBT was spin-coated on oriented iPP; (d) rod-like crystal precursors formed in the C8-BTBT film through SVA; (e) further development of an oriented single crystal array with high quality during SVA; and (f) fabrication of devices on the single crystal array by thermal evaporation with the help of a mask.

Procedures for device array fabrication of single crystals

Fig. 1 shows the procedure for preparing the oriented crystal array. Firstly, a highly oriented iPP thin film prepared by the melt-draw technique was attached on the surface of a cleaned substrate carefully (Fig. 1a and b). Then a solution of C8-BTBT in chloroform was spin-coated on the oriented iPP surface (Fig. 1c). SVA has been achieved with a homemade apparatus

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Results and discussion

Crystal growth on the oriented iPP film

Polymer auxiliary dielectrics facilitate a good balance between insulating characteristics and compatibility with organic semiconductors.²⁸ Herein, a highly oriented iPP film has been obtained by the melt-draw technique with a homemade experimental apparatus shown in Fig. S2 (ESI†). The morphology of the melt-drawn iPP film is characterized by polarized optical microscopy (POM) and atomic force microscopy (AFM). As shown in Fig. 2a, the melt-drawn iPP film exhibits a relative smooth surface topology and a high degree of molecular chain orientation along the drawing direction as confirmed by the electron diffraction with the appearance of sharp and well defined reflection spots (see the inset of Fig. 2a). The AFM phase image (Fig. 2b) shows a highly oriented lamellar structure with the



Fig. 2 (a) POM of a highly oriented iPP film with the corresponding electron diffraction inserted; (b) the phase image of AFM for a highly oriented iPP film and a corresponding partial enlarged image inserted; and (c) cross-sectional SEM image of the sample with the edge of the iPP film indicated by the dashed white lines, showing the iPP film with a thickness of 80 nm. (d) POM of the single crystal array; (e) AFM image of single crystals; (f) height profile of the single crystal at the white line in (e); low (g) and high (h) magnification SEM images of the C8-BTBT single crystals with (h) corresponding to the red frame area in (g); and (i) XRD pattern of the crystal array on the iPP film. The solid white arrows indicate the molecular chain directions of the iPP film.

lamellae arranged perpendicular to the drawing direction, indicating an alignment of the iPP chains or chain segments along the drawing direction. Moreover, the AFM topographical image (Fig. S3, ESI[†]) shows an ideal average roughness of *ca.* 2.5 nm and a maximum difference of ca. 18 nm in topography. As shown in Fig. 2c, cross-sectional scanning electron microscopy (SEM) was conducted to estimate the thickness of the oriented iPP film. The edges of the iPP film are highlighted by a dashed white line and the thickness is measured to be ca. 80 nm. After learning about the structure of the iPP film, the C8-BTBT solution with chloroform as solvent was spin-coated on the surface of the oriented iPP and the octadecyltrichlorosilane (OTS) modified silicon wafer, respectively, for comparing the different crystalline morphologies. After 4 h SVA treatment, semiconductor crystals were obtained on both substrates as shown in Fig. 2d and Fig. S4 (ESI[†]). Compared with the random orientation of C8-BTBT crystals on the OTS modified substrate, it was found that the crystals in the field of view are predominately oriented along the iPP molecular chain direction in regular shape with a length of up to $190 \,\mu m$. The well-developed crystal with a height of 550 nm has a flat surface with neat edges (Fig. 2f). Some of the epitaxially grown C8-BTBT crystals remain at a small angle to the iPP chain

direction (Fig. 2d and e). These results indicate that the growth of the oriented crystals C8-BTBT by an epitaxial method is feasible. In Fig. 2g and h, the SEM images in different scales show that the C8-BTBT crystals on the iPP film have preferred orientation and periodic arrangement. The area inside the red box in Fig. 2g is enlarged to observe the fine structure of the crystals, as shown in Fig. 2h. The C8-BTBT crystals in regular shapes are mainly oriented along the iPP molecular chain direction. Thin film X-ray diffraction (XRD) tests were carried out on the samples and the diffraction peaks were indexed (Fig. 2i). It was found that strong (002) and (003) diffraction peaks of C8-BTBT can be observed, which demonstrate a *c*-axis orientation of C8-BTBT, *i.e.*, the *a*- and *b*-axes arranged in the film plane.

Orientation characterization and statistics of the crystal arrays

Fig. 3 shows the crystal development process of C8-BTBT during SVA on the OTS modified silicon wafer and oriented iPP film, respectively. As presented in Fig. 3a, spin-coating of C8-BTBT on the OTS modified silicon wafer leads to the formation of thin films with a point-like pattern. The subsequent SVA process results in the change in the C8-BTBT structure, as illustrated by Fig. 3b–e. As the SVA proceeds



Fig. 3 Time-dependent structural evolution of C8-BTBT during SVA on an OTS modified wafer (a-e) and on an oriented iPP thin film (g-k) revealed by POM. (f) and (l) show the statistics of the crystal orientation with respect of the iPP chain direction in (d) and (k), respectively. The solid white arrows indicate the molecular chain directions of the iPP films.

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gradually, the number of C8-BTBT crystals decreases accordingly. This indicates the merging process of the C8-BTBT microcrystallites. After 4 h of SVA, as shown in Fig. 3e and Fig. S5 (ESI[†]), large single crystals with flat surfaces and straight edges form. The height of the final crystals is measured to be ca. 300 nm. It is evident that the C8-BTBT single crystals formed on the OTS modified silicon wafer exhibit no preferred orientation. Since the crystal number of the final stage in Fig. 3e is too small to provide the statistics of the crystal orientation, Fig. 3d with relatively more crystals is selected to analyze the statistics of the crystal orientation. As shown in Fig. 3f, 46 single crystals in the field of view show no evident preferred orientation. Actually, a similar spot-shaped pattern was also observed when spin coating the C8-BTBT solution on the oriented iPP substrate (Fig. 3g). However, the evolution of its crystalline morphology during SVA is quite different from that on the OTS modified silicon wafer, comparing Fig. 3b-e and h-k. Several aspects should be addressed here. First, as presented in Fig. 3h, short needle-like crystals with preferred orientation can be observed after only 1 h SVA. The short needle-like crystals are predominately oriented along the molecular chain direction of iPP. Second, these needle-like crystals get also larger and larger with increasing SVA time. The dimension of the oriented C8-BTBT crystals is, however, relatively smaller with respect to those formed on the OTS modified silicon wafer under the same SVA treatment conditions. Third, the number of C8-BTBT crystals generated on the oriented iPP film is much bigger than that on the OTS modified silicon wafer. This reflects that iPP exhibits nucleation ability toward C8-BTBT, which produces more active nuclei but reduces the crystal size of C8-BTBT. Fig. 31 shows the statistical orientation diagram of the 97 crystals distributed in Fig. 3k. It can be clearly seen that around 78% percent of the C8-BTBT crystals are arranged in the molecular chain direction (within $\pm 15^{\circ}$) of iPP. As a result, a highly orientated crystal array of C8-BTBT has been successfully fabricated.

Fabrication and tests of devices based on the arrays

The above experimental results demonstrated that the oriented iPP auxiliary film can promote the oriented self-assembly of C8-BTBT during SVA. It is most likely based on the heteroepitaxy of C8-BTBT on the iPP film. The exact origin of the oriented arrangement of C8-BTBT on the oriented iPP is not clear at the moment and will be studied in detail. We here focus mainly on the impact of the ordered structure on the performance of related devices. For this purpose, OFET devices based on the well-ordered C8-BTBT single crystal array were fabricated (Fig. 4a). The electrode was directly constructed by thermal evaporation with an electrode mask covering the crystal array. The inset of Fig. 4a shows the POM image of an individual device. OFET tests were performed on 100 adjacent devices and 81 of them were valid. Fig. 4c and d show the transfer and output curves of the highest performance device with a mobility of 9.3 cm² V⁻¹ s⁻¹ and an on/off ratio of 10⁷. Counting the effective device mobility and threshold voltage of 81 devices out of 100, as shown in Fig. 4b and Fig. S6 (ESI⁺),



Fig. 4 (a) Configuration of the single-crystal FET array. Inset shows the photo of the channel region in a single device. (b) FET mobility (μ_{FET}) performance of 81 working single crystal FETs out of 100 measured ones in the histogram. (c) Transfer characteristics of a typical device (μ_{FET}) 9.3 cm² V⁻¹ s⁻¹, on/off ratio 10⁷) operated at -60 V drain voltage in air. The effective channel length *L* = 34.8 µm and channel width *W* = 10.9 µm. (d) Output characteristics. Gate voltage (V_{GS}) ranged from 0 to -60 V in -15 V steps.

the average mobility of the devices was calculated to be 2.5 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, which basically realized the array preparation of functional single crystal devices. However, the threshold voltage is relatively high and obtained at ca. 20 V, which may be due to intrinsic carrier traps on the polymer surface, big size variations of the crystals^{29,30} and the poor contact with the substrate¹¹ caused by the large roughness of the polymer layer. In addition, as the processing time increases, the trapping centers for the injected minority charge carriers appear in the channel region due to water/oxygen doping, leading to degradation of device ideality.³¹ And finally, since the oriented iPP film retains some stress during the preparation process, the iPP surface may generate cracks during the stress release process, which may also affect the device performance to some extent. For comparison, the crystals on the OTS modified substrate were prepared for the device fabrication in the same manner as shown in Fig. S7a (ESI[†]). We found that most of the devices were invalid as the crystals distributed randomly failed to bridge the electrodes (Fig. S7b, ESI[†]). The OFET performance test was performed with the less 10% working devices (Fig. S7c, ESI[†]). The typical transfer curve and output curve are shown in Fig. S8a and b (ESI†), and the average mobility is 3.3 cm² V⁻¹ s⁻¹. The huge contrast in the device yield and the comparable mobilities of the devices both on oriented iPP and OTS modified substrates proves that the OFET array fabrication process by oriented epitaxial growth is reliable.

Conclusions

In summary, oriented iPP films were employed as epitaxial growth substrates, on which highly oriented C8-BTBT single

crystal arrays were grown by the SVA method. Moreover, electrodes were prepared by thermal evaporation to realize OFET devices based on the oriented crystal arrays. They have a yield of up to 81%, an average mobility of $2.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with the best mobility of $9.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and an on/off ratio of 10^7 . However, there is plenty of room to optimize, especially in terms of the iPP film morphology, substrate bonding, orientation status, and film stability. Next, we are going to improve these issues and further utilize oriented organic semiconductor crystals on polymer films to achieve flexible device and wearable device construction.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- 1 H. Li, B. C. K. Tee, J. J. Cha, Y. Cui, J. W. Chung, S. Y. Lee and Z. Bao, *J. Am. Chem. Soc.*, 2012, **134**, 2760.
- 2 Y. Zhou, T. Lei, L. Wang, J. Pei, Y. Cao and J. Wang, *Adv. Mater.*, 2010, 22, 1484.
- 3 G. Wu, C. Chen, S. Liu, C. Fan, H. Li and H. Chen, *Adv. Electron. Mater.*, 2015, **1**, 1500136.
- 4 C. Fan, A. P. Zoombelt, H. Jiang, W. Fu, J. Wu, W. Yuan, Y. Wang, H. Li, H. Chen and Z. Bao, *Adv. Mater.*, 2013, 25, 5762.
- 5 J. A. Lim, H. S. Lee, W. H. Lee and K. Cho, *Adv. Funct. Mater.*, 2009, **19**, 1515.
- 6 H. Chen, M. Li, Z. Lu, X. Wang, J. Yang, Z. Wang, F. Zhang,
 C. Gu, W. Zhang, Y. Sun, J. Sun, W. Zhu and X. Guo, *Nat. Commun.*, 2019, 10, 3872.
- 7 A. Kumatani, C. Liu, Y. Li, P. Darmawan, K. Takimiya, T. Minari and K. Tsukagoshi, *Sci. Rep.*, 2012, 2, 393.
- 8 C. R. Kagan, Chem. Soc. Rev., 2019, 48, 1626-1641.
- 9 H. Chen, N. Cheng, W. Ma, M. Li, S. Hu, L. Gu, S. Meng and X. Guo, *ACS Nano*, 2016, **10**, 436.
- 10 J. Qian, S. Jiang, S. Li, X. Wang, Y. Shi and Y. Li, *Adv. Mater. Technol.*, 2019, 4, 1800182.

- 11 C. Liu, T. Minari, X. Lu, A. Kumatani, K. Takimiya and K. Tsukagoshi, *Adv. Mater.*, 2011, 23, 523.
- 12 J. Huang, Y. Qian, K. Evans and T. Xu, *Macromolecules*, 2019, 52, 5801.
- 13 C. Sinturel, M. Vayer, M. Morris and M. A. Hillmyer, *Macro-molecules*, 2013, 46, 5399.
- 14 H. Chen, S. Dong, M. Bai, N. Cheng, H. Wang, M. Li, H. Du, S. Hu, Y. Yang, T. Yang, F. Zhang, L. Gu, S. Meng, S. Hou and X. Guo, *Adv. Mater.*, 2015, 27, 2113.
- 15 Y. Huang, D. L. Elder, A. L. Kwiram, S. A. Jenekhe, A. K. Y. Jen, L. R. Dalton and C. K. Luscombe, *Adv. Mater.*, 2019, 1904239.
- 16 Z. He, J. Chen and D. Li, J. Vac. Sci. Technol., A, 2019, 37, 040801.
- 17 Y. Yuan, G. Giri, A. L. Ayzner, A. P. Zoombelt, S. C. B. Mannsfeld, J. Chen, D. Nordlund, M. F. Toney, J. Huang and Z. Bao, *Nat. Commun.*, 2014, 5, 3005.
- 18 E. Uchida, R. Azumi and Y. Norikane, *Nat. Commun.*, 2015, 6, 7310.
- 19 T. Izawa, E. Miyazaki and K. Takimiya, *Adv. Mater.*, 2008, **20**, 3388.
- 20 L. Ma, J. Zhang, M. A. Memon, X. Sun, H. Li and S. Yan, *Polym. Chem.*, 2015, **6**, 7524.
- 21 Q. Liu, X. Sun, H. Li and S. Yan, Polymer, 2013, 54, 4404.
- 22 G. Guan, J. Zhang, X. Sun, H. Li, S. Yan and B. Lotz, Macromol. Rapid Commun., 2018, 39, 1800353.
- 23 S. Yan and J. Petermann, Polymer, 2000, 41, 6679-6681.
- 24 Y. Li, C. Liu, A. Kumatani, P. Darmawan, T. Minari and K. Tsukagoshi, *Org. Electron.*, 2012, **13**, 264.
- 25 S. Kwon, J. Kim, G. Kim, K. Yu, Y.-R. Jo, B.-J. Kim, J. Kim, H. Kang, B. Park and K. Lee, *Adv. Mater.*, 2015, 27, 6870.
- 26 R. Janneck, N. Pilet, S. P. Bommanaboyena, B. Watts,
 P. Heremans, J. Genoe and C. Rolin, *Adv. Mater.*, 2017,
 29, 1703864.
- 27 X. Liu, X. Luo, H. Nan, H. Guo, P. Wang, L. Zhang, M. Zhou,
 Z. Yang, Y. Shi, W. Hu, Z. Ni, T. Qiu, Z. Yu, J.-B. Xu and
 X. Wang, *Adv. Mater.*, 2016, 28, 5200.
- 28 D. Ji, T. Li, Y. Zou, M. Chu, K. Zhou, J. Liu, G. Tian, Z. Zhang, X. Zhang, L. Li, D. Wu, H. Dong, Q. Miao, H. Fuchs and W. Hu, *Nat. Commun.*, 2018, 9, 2339.
- W. Deng, X. Zhang, H. Dong, J. Jie, X. Xu, J. Liu, L. He, L. Xu,
 W. Hu and X. Zhang, *Mater. Today*, 2019, 24, 17.
- 30 X. Zhang, J. Mao, W. Deng, X. Xu, L. Huang, X. Zhang, S.-T. Lee and J. Jie, *Adv. Mater.*, 2018, **30**, 1800187.
- 31 X. Wu, R. Jia, J. Jie, M. Zhang, J. Pan, X. Zhang and X. Zhang, *Adv. Funct. Mater.*, 2019, 1906653.