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Supplementary Information

Directional lateral crystallization of vacuum-deposited C8-BTBT thin films via liquid crystal phase by a seeded horizontal temperature gradient cooling technique

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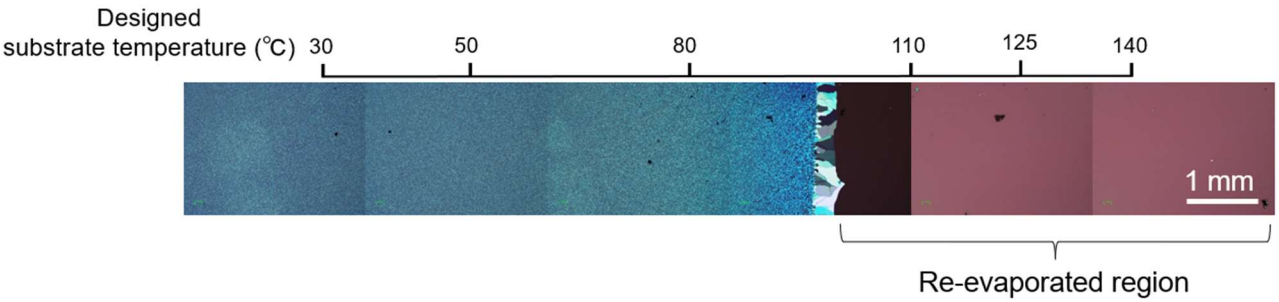

Fig. S1 Stitched POM images for a C8-BTBT thin film deposited at room temperature and subsequently post-annealed with temperature gradient in vacuum. The thin film was re-evaporated by the post-annealing at the designed substrate temperature of >100 °C.

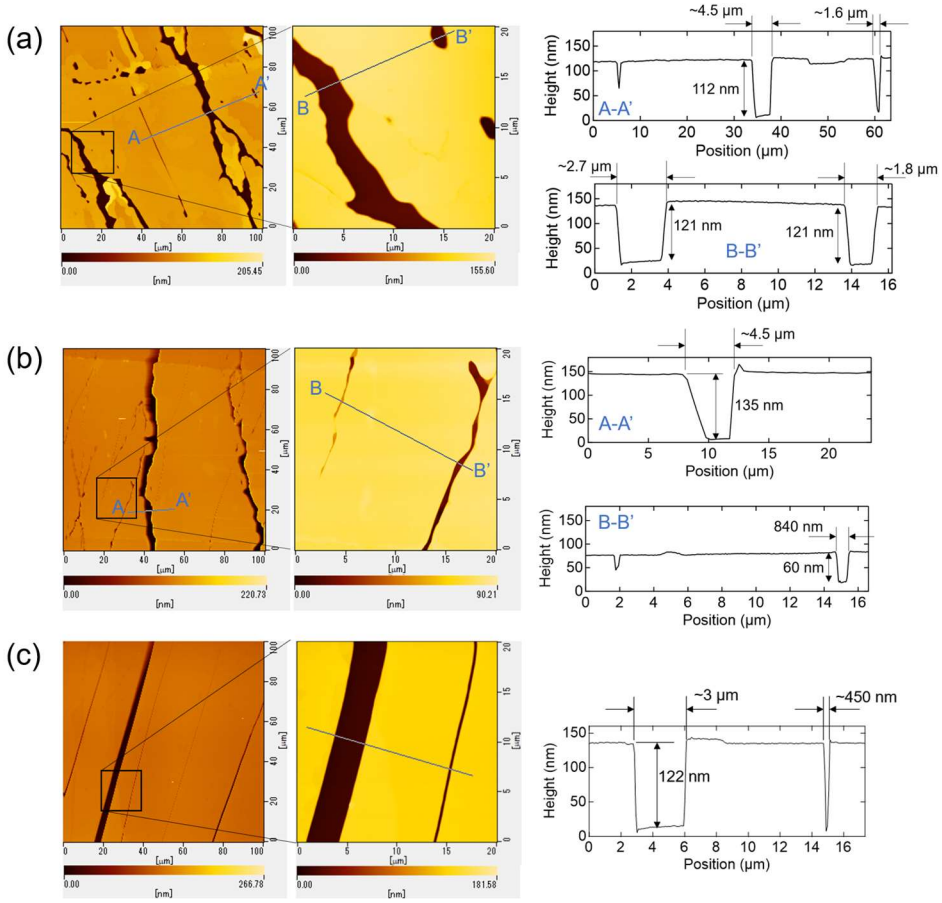

Figure S2. AFM images and their profiles of the samples (a) cooling from a uniform temperature of 120 °C, (b) 110-120 °C temperature gradient, and (c) 107-117 °C temperature gradient, corresponding to the samples shown in Fig. 4(a)-(c), respectively. In all these images, wide cracks with a gap width of several micrometers and narrow cracks with a gap width of <1 micrometer were observed. Most of the cracks observed in the thin films grown by uniform temperature and temperature gradient without seeding were meandering and fragmented; on the other hand, the cracks in the thin film grown by temperature gradient with seeding were straight and connected continuously, at least within this observation scale. This difference could be explained as follows: in the former cases, the cracks formed just after the crystallization as shown in Fig.3(b) and (d). As a result, the shape of the cracks reflects the shape of the growth front fluctuation. In the latter case, on the other hand, the cracks formed after the whole area of the thin film was crystallized, where the energetically favorable crystallographic plane, i.e., the (010) plane would be preferentially broken by the tensile stress almost uniformly accommodated in the thin film. Moreover, interestingly, the depth of the narrow cracks seems to be lower than those of the wider ones as seen in the line profile in (b). This suggests that the thin film layers are also formed at the bottom of the cracks, i.e., the cracks are not penetrated throughout the film along the thickness direction. In fact, the OFET operation was observed in the devices even with a crack angle of 0°, which result supports that thin film layers are also formed at the bottom of the cracks even for the wider cracks.

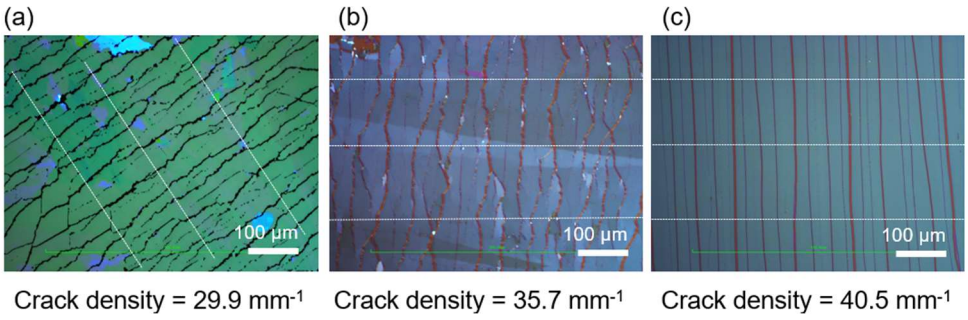

Fig. S3 Magnified POM images of the samples (a) cooling from a uniform temperature of 120 °C, (b) 110-120 °C temperature gradient, and (c) 107-117 °C temperature gradient, corresponding to the samples shown in Fig. 4(a)-(c), respectively, with crack density values which was estimated by dividing the average channel crack count on three lines (white dotted lines) approximately perpendicular to the cracks in each image by the line length.

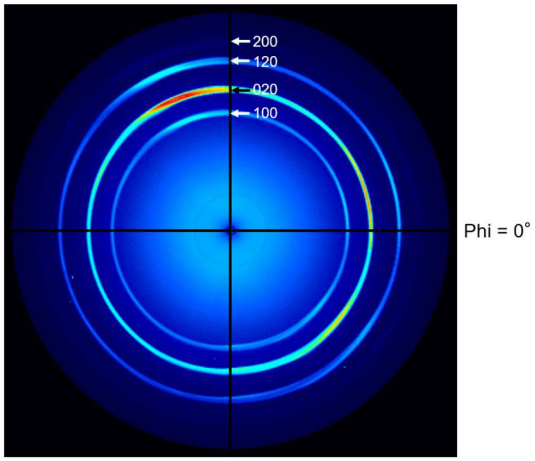

Fig. S4 In-plane reciprocal space maps for as-deposited C8-BTBT thin films at room temperature.

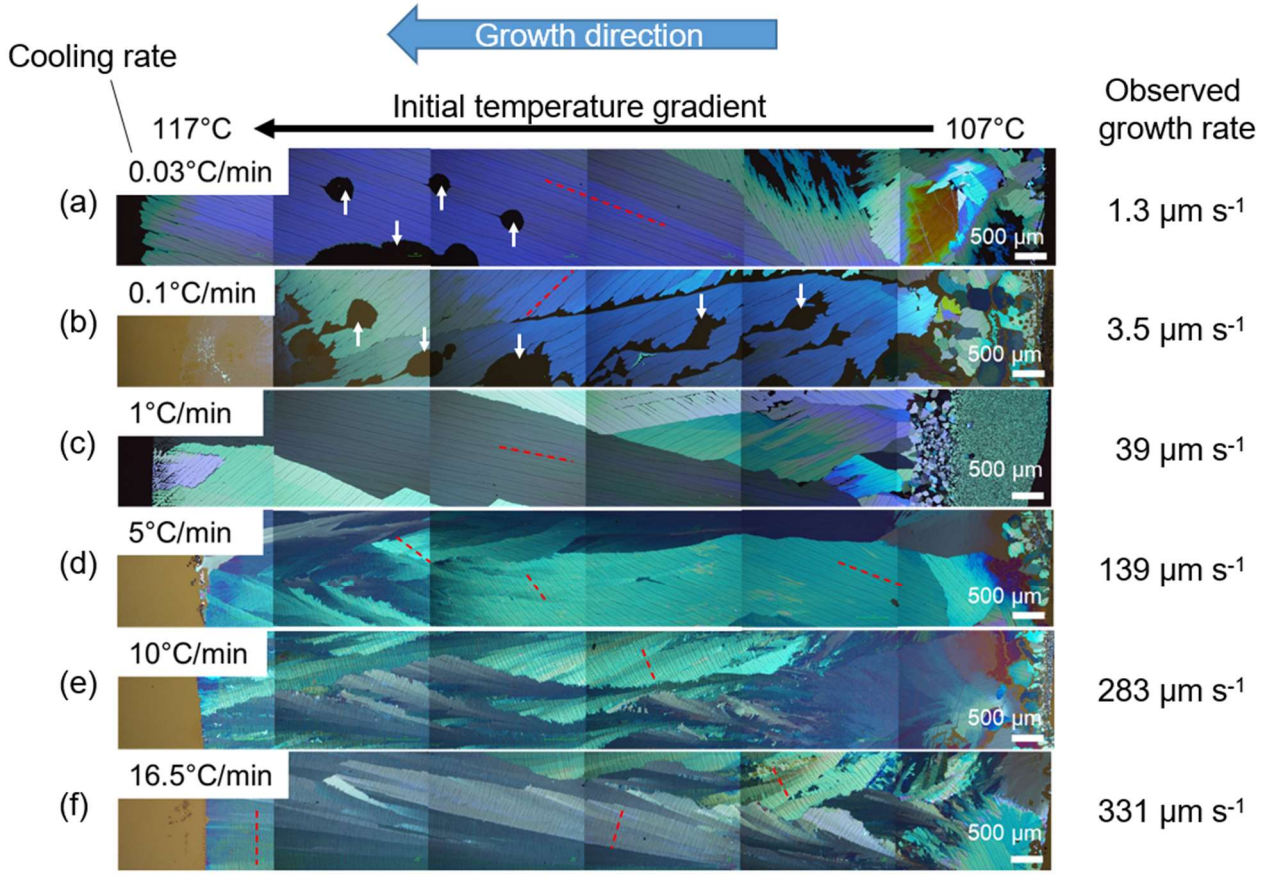

Fig. S5 Stitched POM images for a C8-BTBT thin film grown by the seeded temperature gradient crystallization from 107-117 °C with different cooling rates of (a) 0.03 (b) 0.1 (c) 1 (d) 5 (e) 10 and (f) 16.5 °C min^{-1}. The direction of cracks is denoted by red dashed line. For the samples grown by the high cooling rates (10 and 16.5 °C min^{-1}), i.e. high growth rate, the cracking directions (denoted by red dashed lines) tend to be perpendicular to the growth direction, which is similar to the behaviour of the sample without seeding (Fig. 4(b) and Fig. 5(c)). Note that circular dark regions in the samples grown with the low cooling rate (0.03 and 0.1 °C min^{-1}) (denoted by white arrow) are dewetted region which might be occurred due to the long time annealing.

Note: Thermal expansion coefficient of Si substrate and C8-BTBT

The thermal expansion coefficient of Si is 2.57×10^{-6} K^{-1} at 293 K and 3.24×10^{-6} K^{-1} at 400 K.[1] On the other hand, that of C8-BTBT calculated from the lattice constants of a single crystal measured at 125-275 K in literature[2] are 7.0×10^{-5} K^{-1} and 1.6×10^{-3} K^{-1} for the a-axis and the b-axis, respectively.

Supplementary references

[1] H. Watanabe, N. Yamada and M. Okaji, *Int. J. Thermophys.*, 2004, **25**, 221–236.

[2] A. van der Lee, G. H. Roche, G. Wantz, J. J. E. Moreau, O. J. Dautel and J.-S. Filhol, *Chem. Sci.*, 2018, **9**, 3948–3956.