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Transient phases during crystallization of solution-processed organic thin films¹ JING WAN, YANG LI, JEFFERY ULBRANDT, Department of Physics, University of Vermont, DETLEF-M SMILGIES, Cornell High Energy Synchrotron Source, JONATHAN HOLLIN, ADAM WHALLEY, Department of Chemistry, University of Vermont, RANDALL HEADRICK, Department of Physics, University of Vermont — We report an in-situ study of 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C₈-BTBT) organic semiconductor thin film deposition from solution via hollow pen writing, which exhibits multiple transient phases during crystallization. Under high writing speed (25 mm/s) the films have an isotropic morphology, although the mobilities range up to 3.0 cm²/V·s. To understand the crystallization in this highly non-equilibrium regime, we employ in-situ microbeam grazing incidence wide-angle X-ray scattering combined with optical video microscopy at different deposition temperatures. A sequence of crystallization was observed in which a layered liquid-crystalline (LC) phase of C₈-BTBT precedes inter-layer ordering. For films deposited above 80°C, a transition from LC phase to a transient crystalline state that we denote as Cr1 occurs after a temperature-dependent incubation time, which is consistent with classical nucleation theory. After an additional ≈ 0.5 s, Cr1 transforms to the final stable structure Cr2. Based on these results, we demonstrate a method to produce large crystalline grain size and high carrier mobility during high-speed processing by controlling the nucleation rate during the transformation from the LC phase.

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Jing Wan
Department of Physics, University of Vermont

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