Using Fluid Dynamics Modeling to Guide the Fabrication of Patterned Shearing Blades for the Solution Deposition of Single-Crystalline Organic Semiconductor Thin Films

Geoffrey C. Martin-Noble
Chemistry and Computer Science, Haverford College

NNIN REU Site: Stanford Nanofabrication Facility, Stanford University, Stanford, CA
NNIN REU Principal Investigator: Professor Zhenan Bao, Chemical Engineering, Stanford University
NNIN REU Mentor: Leo Shaw, Chemical Engineering, Stanford University
Contact: gmngeoffrey@gmail.com, zbao@stanford.edu, leoshaw@stanford.edu

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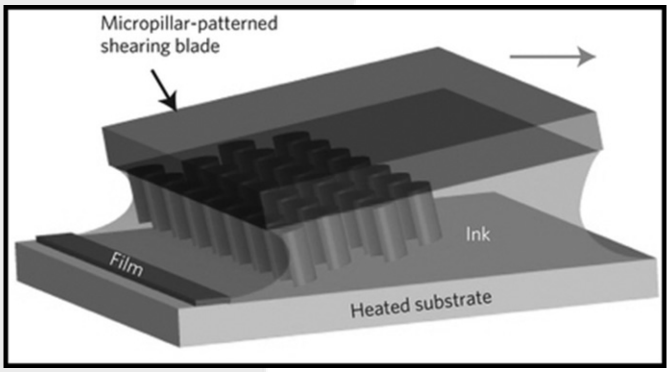

Figure 1: The solution shearing technique using a blade with micro-pillars (not to scale).

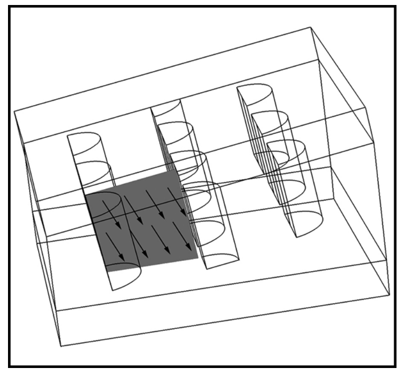

Figure 2: COMSOL model geometry. The trapezoid surface was used to measure mass flux and was not part of the model geometry.

Abstract and Introduction:

Organic semiconductors (OSCs) are promising materials for applications requiring flexible and transparent electronics and have the potential to be produced using low-cost solution processing methods [1, 2]. However, typical solution-based techniques create polycrystalline OSC thin films unable to reach the performance of single crystals grown by vapor-based deposition methods [3].

Previously, the Bao group has developed a method called solution shearing for the deposition of high quality OSC thin films for use in field effect transistors [3]. In solution shearing, the OSC is dissolved in a solvent, and the solution is spread across a heated silicon substrate by a blade moving at a constant velocity, as shown in Figure 1. The solvent evaporates as it is sheared, depositing the OSC solute as a thin film.

Using this technique to shear a solution of 6,13-bis(triisoprop ylsilylethynyl) pentacene (TIPS-pentacene) in toluene resulted in thin films with field effect mobilities—the primary measure of semiconductor effectiveness—more than double the highest previously reported for TIPS-pentacene [4]. However, the films had large void spaces between crystalline ribbons. We suspected that these voids formed because as crystals grow on either side of a region, they pull solute from it, creating a zone with depleted OSC.

To eliminate these voids, micropillars were introduced to the blades [1] (see Figure 1) to induce recirculation in the solution during shearing. This modification virtually eliminated voids and resulted in mobilities double again those achieved without micropillars. Further improvement could likely be achieved by optimization of the micropillar pattern.

In order to better understand the shearing process, we used COMSOL Multiphysics to model the effects of different micropillar shapes and spacings on the solution flow during shearing. We fabricated these blades using photolithography with the aim of correlating simulated fluid flow with experimental blade performance, and thus enabling the use of modeling for future blade development.

Procedure:

Model Parameters. Figure 2 shows the model geometry used in COMSOL. Only the solvent was modeled, as the concentration of OSC is low enough to not affect viscosity. Periodic boundary conditions were used on the sidewalls to model an infinite array of pillars. The mass flux flowing through the system was set to the experimentally determined solvent evaporation rate. To simplify the calculation, the

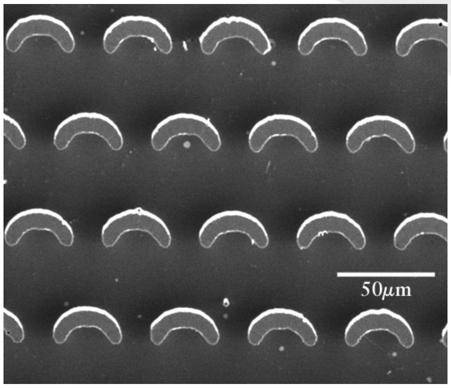

Figure 3: A scanning electron micrograph of part of a completed blade.

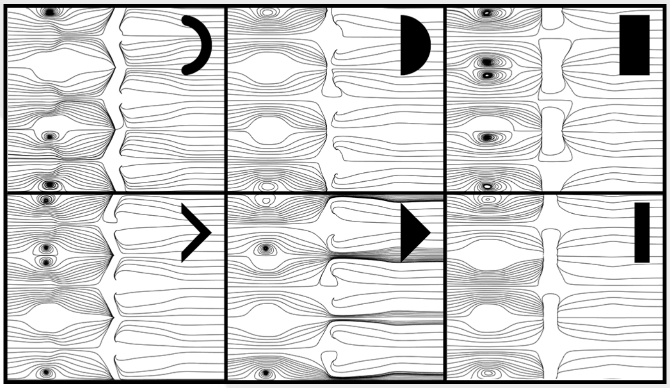

Figure 4: Velocity streamlines of simulated fluid flow. Line spacing indicates speed.

simulation was performed in the frame of reference with the blade stationary and the substrate moving to the left, but all data was adjusted back to the laboratory frame for analysis.

Fabrication of Blades. The blades were created using a standard photolithography procedure and deep reactive ion etching with sulfur hexafluoride (SF_6) on a silicon substrate.

Results and Discussion:

Figure 4 shows two-dimensional velocity streamlines of the simulated fluid flow for different pillar shapes. We also examined different pillar spacings (not shown). The flow is shown 3 μm above the substrate. To try to quantitatively evaluate the different pillar shapes, we measured the simulated lateral mass flux between two rows of pillars through the surface shown in Figure 2. We hypothesized that an increased lateral flux would be an indication of improved recirculation and therefore improved crystals. Flux measurements were 109 ng/s for the model with crescent pillars, 115 ng/s for the chevron, 115 ng/s for the thick bar, 119 ng/s for the thin bar, 123 ng/s for the semicircle, and 125 ng/s for the triangle.

Previous experimental results indicate that the chevron and crescent pillars create noticeable improvements in the TIPS-pentacene thin film, while the semicircle and bar pillars do not. However, the crescent and chevron models actually have the lowest lateral mass flux, so measuring flux across the surfaces we used does not appear to be an effective metric for evaluating the simulations. Neither can we conclude the reverse trend—lower lateral flux improves film quality—because a lateral flux of zero would result from the removal of the micropillars, which were already shown to create a significant improvement.

Summary and Future Work:

Solution shearing has already been demonstrated as an effective method for the creation of high-quality single-crystalline OSC thin films and the addition of micropillars further improves the technique. However, we cannot use lateral flux as we have measured it in order to effectively evaluate simulation results, so we must identify another figure of merit.

To investigate this project further, we must evaluate the quality of TIPS-pentacene thin films sheared with different blades. We can examine the films optically, employ grazing incidence x-ray diffraction to calculate crystal coherence length, and measure the field-effect mobilities of the films. By correlating experimental and simulation results, we aim to find an effective metric for evaluating simulation results. With appropriate evaluation, the simulations can be used to determine optimal pillar patternings for a range of different systems.

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References:

[1] Gao, P., et al. Adv. Mater. 21, 213-216 (2009).

[2] Rogers, J. A., et al. Proc. Natl. Acad. Sci. USA 98, 4835-4840 (2001).

[3] Diao, Y., et al. Nat. Mater. 12, 665-671 (2013).

[4] Giri, G., et al. Nature 480, 504-508 (2011).