Supporting Information for:

Leveraging Process Fundamentals to Improve Semiconductor Thickness Control and Uniformity in Inkjet-Printed Schottky Diodes

Jonathan D. Nguyen, Satish Kumar, C. Daniel Frisbie*, Lorraine F. Francis*

Department of Chemical Engineering and Materials Science, University of Minnesota, 421 Washington Avenue SE, Minneapolis, MN 55455, United States of America

E-mail: *lfrancis@umn.edu; *frisbie@umn.edu

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S1. Silicon Template Wafer Fabrication Details

To fabricate the mesa diode design on a silicon template wafer, two cycles of photolithography were completed to pattern the two levels within the design. First, the pristine wafer was dehydrated at 150°C for 3 min on a hotplate. The wafer was then exposed to a hexamethyldisilazane (HMDS) atmosphere for 3 min. to improve photoresist adhesion. Positive photoresist (AZ1512, MicroChemicals GmbH) was spin-coated (3000 rpm, 3000 rpm/s, 30 s) onto the wafer followed by a soft bake (100°C, 1 min). The wafer was placed into a photomask aligner (Karl Suss MA6) and exposed to ultraviolet light (12 mW/cm²) for 5 s, followed by a post-exposure bake (95°C, 1 min). The exposed wafer was developed (1:5 by volume of AZ340 Developer:H₂O) for 30 s to remove the exposed photoresist. The exposed silicon surface was etched to a depth of 5 μm using a deep trench etcher (SPTS Rapier) system to pattern the reservoirs and capillary channels. Etch depths and feature heights were verified using stylus profilometry (KLA Tencor P-
7). The remaining photoresist was removed with sequential acetone, methanol, isopropanol, and water rinsing followed by sonication in an acetone bath before drying the wafer in a N$_2$ stream.

To pattern the second layer, the same wafer underwent a second cycle of photolithography. The wafer was cleaned in an O$_2$ plasma chamber (200 W RF power, 200 sccm O$_2$ gas flow, 10 min.) to remove any residual photoresist from the previous step. A 4 μm thick layer of permanent epoxy negative photoresist (SU-8 2005, Kayaku Advanced Materials) was spin coated (2700 rpm, 300 rpm/s, 30 s) onto the wafer, followed by a soft bake (95°C, 2 min). The second layer pattern was aligned to the previous layer and the wafer was exposed for 9 s followed by a post-exposure bake (95°C, 3 min). The exposed photoresist crosslinked and permanently bonded to the wafer, while the unexposed photoresist was washed away in developer solution (SU-8 Developer, Kayaku Advanced Materials) for 15 s. After rinsing with isopropanol and N$_2$ drying, the wafer template was finished with a hard bake (150°C, 30 min.) on a hotplate.
Figure S2. Detailed dimensions of the mesa diode design structural features and overall geometry from top-down and cross-sectional views. All dimension labels denote units in microns. Note: schematic is not drawn to scale.
S3. Optical micrographs of the device during fabrication

**Figure S3.** Optical micrographs of the mesa diode after each fabrication step: (a) UV microimprinting, (b) Ag printing and annealing, (c) P3HT printing and drying, (d) PEDOT:PSS printing and drying. Panels (c,d) zoom in on the diode’s central device region for further detail.
S4. Contact angle measurements

Figure S4. Measured contact angle of a drop of 1,2-dichlorobenzene on UV cured resin NOA73. The droplet volume deposited was approximately 4 μL. The measurement was taken using a Kruss DSA-30S drop shape analyzer.
S5. Surface tension measurements

Figure S5. (a) Surface tension measurements on solutions of P3HT dissolved in 1,2-dichlorobenzene with varying P3HT concentrations. Data points represent average values, while error bars indicate standard deviation. Measurements were taken using the pendant drop method. (b) Photograph of the as-prepared P3HT solutions ranging from least to most concentrated going from left to right.
S6. Estimation of Péclet Number, $Pe$, for the P3HT solution drying on the mesa:

Prior reports in the literature\textsuperscript{1-3} exploring the coffee ring effect define the Péclet number:

$$Pe = \frac{\text{Advection}}{\text{Diffusion}} = \frac{v(T)}{D(T)} l \tag{1}$$

where $v$, $D$, $l$, and $T$ are the advection velocity, the solute diffusivity, the characteristic length, and the temperature. The advection velocity is the lateral velocity of the solute toward the pinned edge of the drying solution droplet on the mesa. This velocity is equal to the rate of the solvent removal by evaporation at the pinned edge. Thus, the advection velocity is directly proportional to the rate of evaporation, as shown below:

$$Pe = \frac{v(T)}{D(T)} l = \frac{\text{Evaporation}}{\text{Diffusion}} = \frac{c E_0(T)}{D(T)} l \tag{2}$$

where $E_0$ is the evaporation rate in volume per unit time per unit surface area and $c$ is a geometric constant that accounts for the enhanced evaporation at the pinned edge. To estimate values for $Pe$, values for evaporation rate and diffusion coefficient are needed.

**Evaporation rate estimation.** The evaporation rate at 23°C and 90°C was found experimentally. Approximately 0.4 mL of a 30 mg/mL solution of P3HT in 1,2-dichlorobenzene (oDCB) was deposited into a 10 mL glass beaker such that the entire bottom surface of the beaker was covered in solution. This beaker was placed onto a balance and the mass loss was recorded over time. For the 23°C drying case, the beaker was kept on the balance for the entire duration while the mass was recorded periodically. For the 90°C drying case, the beaker was placed on a hotplate set to 90°C and was periodically placed on the balance to measure the mass, after which the beaker was returned to the hotplate to continue evaporation. The results are shown in Figure S7. Two trials were conducted under each temperature condition. To examine if the presence of solute has a noticeable influence on the rate of mass loss, the experiment was repeated, this time
Figure S7. Measured mass loss for a solution of 30 mg/ml P3HT dissolved in 1,2-dichlorobenzene from solvent evaporation over time at (a) 23°C and (b) 90°C. The inset shows a cartoon schematic of the sample material and liquid level in the beaker.

with ~0.4 mL of pure oDCB. The results are shown in Figure S8. The measured rate of mass loss with the pure oDCB solvent was nearly identical to that of the P3HT solution dissolved in oDCB, as exhibited by the matching slope values between Figures S7 and S8. Thus, the presence of solute does not appear to influence the evaporation rate in the initial stages of drying.
Figure S8. Measured mass loss for ~0.4mL of 1,2-dichlorobenzene in a 10 mL beaker due to solvent evaporation over time at (a) 23°C and (b) 90°C drying temperature. The inset shows a cartoon schematic of the sample material and liquid level in the beaker.

With only 0.4 mL of solution in the beaker, the liquid surface was well below the top of the beaker and hence the beaker walls may limit air flow and lower the evaporation rate relative to that experienced on the mesa during device fabrication. To circumvent this effect and better replicate the drying conditions during device fabrication, the beaker was filled with ~10 mL of oDCB solvent and the experiment was repeated. The results are summarized in Figure S9. As expected, the evaporation rate was higher in this configuration as indicated by a steeper slope. In the 90°C drying case, the time interval between measurements was varied from 0.5 – 2 min. When longer intervals were used, the measured evaporation rate was slightly higher than those found at the shorter intervals, likely because the longer measurement interval minimized the slight cooling that occurs when the sample is removed from the hot plate briefly for the measurement. Therefore, the evaporation rate for the data collected with 2 min time interval was used.
Figure S9. Measured mass loss for ~10 mL of 1,2-dichlorobenzene in a 10 mL beaker due to solvent evaporation over time at (a) 23°C and (b) 90°C drying temperature. For the 90°C drying case, four trials were conducted with different time intervals between measurements ranging from 0.5, 1, and 2 minutes. The inset shows a cartoon schematic of the sample material and liquid level in the beaker.

The average rate of mass loss over time was obtained as the slope of the fitted line in each trial. For the 23°C drying case, a slope of $4.1 \times 10^{-4}$ g/min was obtained. Using the density of oDCB at 23°C (1.3 g/cm$^3$), the mass loss was converted into a volumetric loss of 0.315 mm$^3$/min. The diameter of the beaker was measured as 25 mm, resulting in a surface area of 491 mm$^2$. Using the values for volumetric loss and area, an evaporation velocity (i.e., the velocity at which the free surface drops) was found to be $1.07 \times 10^{-6}$ cm/s $\sim 0.01$ µm/s. Likewise for the 90°C drying, the slope gives a mass loss of 0.005 g/min. Using the density of oDCB at 90°C (1.23 g/cm$^3$), the mass loss was converted into a volumetric loss of 4.07 mm$^3$/min and the evaporation velocity was found to be $1.38 \times 10^{-5}$ cm/s $\sim 0.14$ µm/s.
Diffusion coefficient estimation. This estimation is based on standard approaches found in polymer textbooks. The Rouse-Zimm model describes an ideal chain in solution as a series of beads connected by harmonic springs. The Stokes-Einstein relation is used to estimate the diffusion coefficient of a polymer chain in a dilute solution:

\[ D = \frac{k_B T}{6\pi \eta_s R_h} \]  

(3)

where \( k_B \) is the Boltzmann constant, \( T \) is absolute temperature in Kelvin, \( \eta_s \) is the solvent viscosity, and \( R_h \) is the hydrodynamic radius of the polymer chain defined as:

\[ R_h = b N^{\nu} \]  

(4)

where \( b \) is the statistical segment length, \( N \) is the number of monomers (degree of polymerization), and \( \nu \) is the Flory exponent, which is assumed to be 0.5 for an ideal chain. For the P3HT in oDCB solution present in this work, \( N \) is approximated as:

\[ N = \frac{60,000 \text{ g mol}^{-1}}{166.28 \text{ g mol}^{-1}} = 361 \]

using the chain molecular weight according to the product specifications (P3HT regioregular electronic grade, Rieke Metals) and the monomer molecular weight. The value of \( b \) is reported as 0.8 nm. Therefore, \( R_h \) and \( D \) are given by:

\[ R_h = (0.8 \text{ nm})(361)^{\frac{1}{2}} = 15.2 \text{ nm} \]

\[ D(T) = \frac{k_B T}{6\pi \eta_s R_h} = \frac{1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1} (T)}{6\pi(\eta_s)(1.52 \times 10^{-8} \text{ m})} \]

For \( T = 23^\circ \text{C} = 296 \text{ K} \), the 1,2-dichlorobenzene viscosity\(^8\) is \( \eta_s = 1.36 \text{ mPa} \cdot \text{s} \) and so:

\[ D(23^\circ \text{C}) = 1.05 \times 10^{-11} \frac{\text{m}^2}{\text{s}} = 1.05 \times 10^{-7} \frac{\text{cm}^2}{\text{s}} \]

For \( T = 90^\circ \text{C} = 363 \text{ K} \), the 1,2-dichlorobenzene viscosity\(^8\) is \( \eta_s = 0.65 \text{ mPa} \cdot \text{s} \) and so:
\[ D(90^\circ C) = 2.69 \times 10^{-11} \, \text{m}^2/\text{s} = 2.69 \times 10^{-7} \, \text{cm}^2/\text{s} \]

**Pe Calculation.** The diffusion coefficient and evaporation rate can now be added to the expression \( Pe \) at the two temperatures:

\[
Pe(23^\circ C) = \frac{cE(23)}{D(23)} \frac{c(1.07 \times 10^{-6} \, \text{cm/s})}{(1.05 \times 10^{-7} \, \text{cm}^2/\text{s})} \frac{1}{l} = 0.23c
\]

\[
Pe(90^\circ C) = \frac{cE(90)}{D(90)} \frac{c(1.38 \times 10^{-5} \, \text{cm/s})}{(2.69 \times 10^{-7} \, \text{cm}^2/\text{s})} \frac{1}{l} = 1.15c
\]

The characteristic length for the case of a drying drop on top of the mesa is \( l = 225 \, \mu\text{m} \), the mesa radius. Due to the curvature of the droplet shape, the surface area of the liquid-air interface is larger compared to a flat liquid surface, which would result in faster evaporation. In this case, a value of \( c > 1 \) is expected to account for that. The two values of \( Pe \) for the mesa are:

\[
Pe(23^\circ C) = \frac{cE(23)}{D(23)} \frac{c(1.07 \times 10^{-6} \, \text{cm/s})}{(1.05 \times 10^{-7} \, \text{cm}^2/\text{s})} \frac{1}{0.0225 \, \text{cm}} = 0.23c
\]

\[
Pe(90^\circ C) = \frac{cE(90)}{D(90)} \frac{c(1.38 \times 10^{-5} \, \text{cm/s})}{(2.69 \times 10^{-7} \, \text{cm}^2/\text{s})} \frac{1}{0.0225 \, \text{cm}} = 1.15c
\]

And the resulting ratio is:

\[
\frac{Pe(90^\circ C)}{Pe(23^\circ C)} = 5
\]
S10. Estimation of Péclet Number, $P_e$, for the P3HT solution drying over channels:

For the solution drying over recessed channels, the same Péclet number (Eqn. 2) as in section S5 can be used to determine the relative effects of evaporation and diffusion:

$$P_e = \frac{\text{Evaporation}}{\text{Diffusion}} = \frac{cE(T)}{D(T)} = \frac{E(T)}{D(T)}$$

In this case, the evaporation rate is uniform over the drying solution free surface; therefore $c = 1$ and the measured evaporation rates can be used directly. The presence of the channels leads to the development of lateral concentration gradient as the free surface of the layer descends at a rate of $E$. The characteristic length is 2.5 μm, half the channel width. Using the information for diffusivity and evaporation rate in section S5, two values for $P_e$ are obtained as follows:

$$P_e(23^\circ C) = \frac{cE(23)}{D(23)} = \frac{(1)(1.07 \times 10^{-6} \text{ cm/s})}{\left(\frac{1.05 \times 10^{-7} \text{ cm}^2}{\text{s}}\right) \left(\frac{2.5 \times 10^{-4} \text{ cm}}{\text{s}}\right)} = 2.6 \times 10^{-3}$$

$$P_e(90^\circ C) = \frac{cE(90)}{D(90)} = \frac{(1)(1.38 \times 10^{-5} \text{ cm/s})}{\left(\frac{2.69 \times 10^{-7} \text{ cm}^2}{\text{s}}\right) \left(\frac{2.5 \times 10^{-4} \text{ cm}}{\text{s}}\right)} = 1.3 \times 10^{-2}$$

and the resulting ratio is:

$$\frac{P_e(90^\circ C)}{P_e(23^\circ C)} = 5$$
Supporting Information References


